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(54) Titre : PROCEDE D'OXYDATION REPOSANT SUR LA TECHNOLOGIE DES MICROCANAUX ET NOUVEAU
CATALYSEUR UTILE DANS LEDIT PROCEDE
(54) Title: OXIDATION PROCESS USING MICROCHANNEL TECHNOLOGY AND NOVEL CATALYST USEFUL IN
SAME

(57) **Abrégé/Abstract:**

A process is disclosed for converting a hydrocarbon reactant to CO and H₂. The process comprises: (A) flowing a reactant composition comprising the hydrocarbon reactant and oxygen or a source of oxygen through a microchannel reactor in contact with a catalyst under reaction conditions to form the product. The product formed in step (A) may be converted to a product comprising CO₂ and H₂O in a microchannel reactor. A catalyst is disclosed which comprises a composition represented by the formula M¹_a M²_b M³_c Al_d O_x wherein: M¹ is Rh, Ni, Pd, Pt, Ru, Co or a mixture of two or more thereof; M² is Ce, Pr, Tb or a mixture of two or more thereof.



Abstract

A process is disclosed for converting a hydrocarbon reactant to CO and H₂. The process comprises: (A) flowing a reactant composition comprising the hydrocarbon reactant and oxygen or a source of oxygen through a microchannel reactor in contact with a catalyst under reaction conditions to form the product. The product formed in step (A) may be converted to a product comprising CO₂ and H₂O in a microchannel reactor. A catalyst is disclosed which comprises a composition represented by the formula $M^1_a M^2_b M^3_c Al_d O_x$ wherein: M¹ is Rh, Ni, Pd, Pt, Ru, Co or a mixture of two or more thereof; M² is Ce, Pr, Tb or a mixture of two or more thereof.

Title: Oxidation Process Using Microchannel Technology and Novel Catalyst Useful in Same

Technical Field

5 This invention relates to an oxidation process using microchannel technology and a novel catalyst useful in the oxidation process.

Background of the Invention

10 Complete combustion of methane and higher order hydrocarbons is difficult to achieve under fuel-rich conditions in microchannel reactors with relatively short contact times. The combustion is incomplete and this leads to undesirable levels of carbon monoxide and carbon deposits. The problem therefore is to find a way in which to conduct a complete combustion reaction in a microchannel reactor. This invention provides a solution to this problem.

15 Partial oxidation reactions typically involve reacting a hydrocarbon with oxygen in the presence of a catalyst to form hydrogen and carbon monoxide. Examples include the conversion of methane to hydrogen and carbon monoxide. A problem with these reactions is that they are exothermic and are typically conducted in fixed bed reactors where hot spots tend to form. The formation of these hot spots increases the tendency of the catalyst to deactivate. This invention provides a solution to this problem.

20 This invention relates to a process wherein a partial oxidation reaction or a partial oxidation reaction coupled with combustion reaction is conducted in a microchannel reactor wherein the tendency to form hot spots is reduced and selectivity to the desired product is enhanced. Reductions in these hot spots with the inventive process is believed to be due at least in part to the fact that the microchannel reactor provides enhanced heat transfer characteristics and more precise control of residence times. In one embodiment, a novel, stable and highly active partial oxidation catalyst is used in the inventive process.

25 With the inventive process it is possible to obtain relatively high heat and mass transfer rates and shorter contact times as compared to prior art processes wherein microchannel reactors are not used. This provides for more precise temperature control as compared to such prior art. This, in turn, leads to an increase in catalyst durability and a reduction in the formation of undesired by-products. With this process, it is possible to

30

obtain relatively high levels of conversion of the hydrocarbon reactant and high levels of selectivity to the desired product as compared to such prior art.

Summary of the Invention

5 In one aspect, there is provided process for converting a hydrocarbon reactant to a product comprising H₂ and CO, the process comprising: (A) flowing a reactant composition comprising the hydrocarbon reactant and oxygen or a source of oxygen through a microchannel reactor in contact with a catalyst under reaction conditions to convert the reactant composition to the product, the
10 hydrocarbon reactant comprising methane, the catalyst comprising a composition represented by the formula



wherein M¹ is Rh, Ni, Pd, Pt, Ru, Co or a mixture of two or more thereof; M² is Ce, Pr, Tb or a mixture of two or more thereof; M³ is La, Ba, Zr, Mg, Ca or a
15 mixture of two or more thereof; a is a number in the range of about 0.0001 to about 1; b is a number in the range of zero to about 0.9999; c is a number in the range of about 0.0001 to about 0.9999; d is a number in the range of about 0.0001 to about 0.9999; and x is the number of oxygens needed to fulfill the valency requirements of the elements present; the catalyst being coated on an
20 interior wall of the process microchannel, or supported on a foam, felt, wad or fin positioned within the process microchannel.

In another aspect, there is provided a catalyst comprising a composition represented by the formula



25 wherein M¹ is Rh, Ni, Pd, Pt, Ru, Co or a mixture of two or more thereof; M² is Ce, Pr, Tb or a mixture of two or more thereof; M³ is La, Ba, Zr, Mg, Ca or a mixture of two or more thereof; a is a number in the range of about 0.0001 to about 1; b is a number in the range of zero to about 0.9999; c is a number in the range of about 0.0001 to about 0.9999; d is a number in the range of about
30 0.0001 to about 0.9999; and x is the number of oxygens needed to fulfill the

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valency requirements of the elements present; the catalyst being coated on a substrate or supported on a foam, felt, wad or fin.

In another aspect, there is provided a catalyst comprising a composition represented by the formula



wherein a is a number in the range of about 0.0001 to about 0.9999; c is a number in the range of about 0.0001 to about 0.9999; d is a number in the range of about 0.0001 to about 0.9999; and x is the number of oxygens needed to fulfill the valency requirements of the elements present.

10 In another aspect, there is provided a process for making a supported catalyst, comprising: (A) applying a layer of Al_2O_3 over at least part of a support structure; (B) calcining the treated support structure formed in step (A); (C) applying a promoter or stabilizer to the surface of the calcined support structure formed in step (B) to form a treated support structure, the promoter or stabilizer
15 comprising La, Ba, Zr, Mg, Ca, or an oxide or nitrate thereof, or a mixture of two or more thereof; (D) calcining the treated support structure formed in step (C); (E) applying a catalytic metal or oxide or nitrate thereof to the surface of the calcined support structure formed in step (D) to form a treated support structure, the catalytic metal comprising Rh, Ni, Pd, Pt, Ru, Co or a mixture of two or more
20 thereof; and (F) calcining the treated support structure formed in step (E) to form the supported catalyst.

This invention also relates to a process for converting a hydrocarbon reactant to a partial oxidation reaction product comprising CO and H_2 in a microchannel reactor, the microchannel reactor comprising at least one process
25 microchannel and at least one partial oxidation reaction catalyst in the at least one process microchannel, the process comprising:

(A) mixing a reactant composition comprising the hydrocarbon reactant and oxygen or a source of oxygen in the at least one process microchannel and flowing the resulting mixture in the at least one process
30 microchannel in contact with the at least one partial oxidation reaction catalyst

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under partial oxidation reaction conditions to form the product, the hydrocarbon reactant comprising methane, the contact time for the reactant composition within the at least one process microchannel being up to about 500 milliseconds, the temperature of the reactant composition and product within the at least one process microchannel being up to about 1150°C, the conversion of the hydrocarbon reactant being at least about 50%.

In one embodiment of the invention, the catalyst used in step (A) is a partial oxidation catalyst, the product formed in step (A) is an intermediate product, and the process further comprises the following additional step subsequent to step (A):

(B) flowing the intermediate product formed in step (A) through a microchannel reactor in contact with a combustion catalyst under reaction conditions to form a final product comprising CO₂ and H₂O.

In one embodiment, the reactant composition further comprises H₂O and the product comprises H₂, CO and CO₂.

In one embodiment, the invention relates to a catalyst comprising a composition represented by the formula



wherein

M¹ is Rh, Ni, Pd, Pt, Ru, Co or a mixture of two or more thereof;

M² is Ce, Pr, Tb or a mixture of two or more thereof;

M^3 is La, Ba, Zr, Mg, Ca or a mixture of two or more thereof;

a is a number in the range of about 0.0001 to about 1;

b is a number in the range of zero to about 0.9999;

c is a number in the range of about 0.0001 to about 0.9999;

5 d is a number in the range of about 0.0001 to about 0.9999; and

x is the number of oxygens needed to fulfill the valency requirements of the elements present;

the catalyst being coated on a substrate or supported on a foam, felt, wad or fin.

10 In one embodiment, the invention relates to a process for making a supported catalyst, comprising:

(A) applying a layer of Al_2O_3 over at least part of a support structure;

(B) calcining the treated support structure formed in step (A);

15 (C) applying a promoter or stabilizer to the surface of the calcined support structure formed in step (B), the promoter or stabilizer comprising La, Ba, Zr, Mg, Ca, or an oxide or nitrate thereof, or a mixture of two or more thereof;

(D) calcining the treated support structure formed in step (C);

20 (E) applying a catalytic metal or oxide or nitrate thereof to the surface of the calcined support structure formed in step (D), the catalytic metal comprising Rh, Ni, Pd, Pt, Ru, Co or a mixture of two or more thereof; and

(F) calcining the treated support structure formed in step (E) to form the supported catalyst.

Brief Description of the Drawings

In the annexed drawings, like parts and features have like designations.

25 Fig. 1 is a schematic flow sheet illustrating the inventive partial oxidation process in a particular form wherein a hydrocarbon reactant and oxygen or a source of oxygen contact the inventive catalyst in a microchannel reactor and react to form a product comprising hydrogen and a carbon oxide.

30 Fig. 2 is a schematic flow sheet illustrating the operation of a particular form of a microchannel reactor used with the inventive partial oxidation process.

Fig. 3 is a schematic illustration of a process microchannel used with the inventive partial oxidation process, the process microchannel containing a catalyst having a flow-by configuration.

5 Fig. 4 is a schematic illustration of a process microchannel used with the inventive partial oxidation process, the process microchannel containing a catalyst having a flow-through configuration.

10 Fig. 5 is a schematic illustration of a process microchannel used in the inventive partial oxidation process, the process microchannel containing a fin assembly comprising a plurality of fins, the inventive catalyst being supported by the fins.

Fig. 6 illustrates an alternate embodiment of the process microchannel and fin assembly illustrated in Fig. 5.

Fig. 7 illustrates an alternate embodiment of the fin assembly illustrated in Fig. 5.

15 Fig. 8 is a plot of process performance versus time for the tests disclosed in Example 2.

Fig. 9 is a plot of process performance versus time for the tests disclosed in Example 7.

20 Fig. 10 illustrates the channel arrangement for the microchannel reactor used in the tests disclosed in Example 8.

Fig. 11 illustrates the fin assembly for the microchannel reactor used in Example 9.

Detailed Description of the Invention

25 The term "microchannel" refers to a channel having at least one internal dimension of height or width of up to about 10 millimeters (mm), and in one embodiment up to about 5 mm, and in one embodiment up to about 2 mm, and in one embodiment up to about 1 mm. In one embodiment, the height or width is in the range of about 0.05 to about 10 mm, and in one embodiment about 0.05 to about 5 mm, and in one embodiment about 0.05 to about 2 mm, and in one
30 embodiment about 0.05 to about 1.5 mm, and in one embodiment about 0.05 to about 1 mm, and in one embodiment about 0.05 to about 0.75 mm, and in one

embodiment about 0.05 to about 0.5 mm. Both height and width are perpendicular to the direction of flow through the microchannel.

5 The term "adjacent" when referring to the position of one channel relative to the position of another channel means directly adjacent such that a wall separates the two channels. This wall may vary in thickness. However, "adjacent" channels are not separated by an intervening channel that would interfere with heat transfer between the channels.

10 The term "fluid" refers to a gas, a liquid, or a gas or a liquid containing dispersed solids, or a mixture thereof. The fluid may be in the form of a gas containing dispersed liquid droplets.

The term "contact time" refers to the volume of the reaction zone within the microchannel reactor divided by the volumetric feed flow rate of the reactant composition at a temperature of 0°C and a pressure of one atmosphere.

15 The term "residence time" refers to the internal volume of a space (e.g., the reaction zone within a microchannel reactor) occupied by a fluid flowing through the space divided by the average volumetric flowrate for the fluid flowing through the space at the temperature and pressure being used.

The term "reaction zone" refers to the space within the microchannel reactor wherein the reactants contact the catalyst.

20 The term "conversion of hydrocarbon reactant" refers to the hydrocarbon reactant mole change between the reactant composition and the product divided by the moles of the hydrocarbon reactant in the reactant composition.

25 The term "selectivity to desired product" refers to the moles of the desired oxygenate or nitrile produced divided by the moles of the desired oxygenate or nitrile produced plus moles of other products (e.g., CO, CO₂) produced multiplied by their respective stoichiometric factors. For example, for the oxidation of ethylene to ethylene oxide with carbon dioxide as an unwanted side product, the production of one mole of ethylene oxide and one mole of carbon dioxide would correspond to a selectivity of $100 \times (1/(1 + 0.5)) = 67\%$.

30 The term "hydrocarbon" denotes a compound having a hydrocarbon or predominantly hydrocarbon character. These hydrocarbon compounds include the following:

(1) Purely hydrocarbon compounds; that is, aliphatic compounds, (e.g., alkane or alkylene), alicyclic compounds (e.g., cycloalkane, cycloalkylene), aromatic compounds, aliphatic- and alicyclic-substituted aromatic compounds, aromatic-substituted aliphatic compounds and aromatic-substituted alicyclic compounds, and the like. Examples include methane, ethane, ethylene, propane, propylene, ethyl cyclohexane, toluene, the xylenes, ethyl benzene, styrene, etc.

(2) Substituted hydrocarbon compounds; that is, hydrocarbon compound containing non-hydrocarbon substituents which do not alter the predominantly hydrocarbon character of the compound. Examples of the non-hydrocarbon substituents include hydroxy, acyl, nitro, etc.

(3) Hetero substituted hydrocarbon compounds; that is, hydrocarbon compounds which, while predominantly hydrocarbon in character, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, oxygen and sulfur.

The inventive process may be conducted as illustrated in Figs. 1 and 2. Referring to Fig. 1, the process is operated using microchannel reactor 100 which includes microchannel reactor core 101, reactant header 102, oxidant header 104, product footer 106, heat exchange header 110 and heat exchange footer 112. The microchannel reactor core 101 includes reactor zone 107, and manifold and recuperator 108. The reactant composition comprising the hydrocarbon reactant flows into the microchannel reactor 100 through the reactant header 102, as indicated by directional arrow 116. The oxygen or source of oxygen flows into the microchannel reactor 100 through the oxidant header 104 as indicated by directional arrow 118. The hydrocarbon reactant and oxygen or source of oxygen flow into and through the manifold and recuperator 108 into the reactor zone 107 wherein they contact the catalyst and react to form the desired product. The product flows from the reactor zone 107 through the manifold and recuperator 108 to product footer 106, and out of product footer 106 as indicated by directional arrow 120. A heat exchange fluid may flow into heat exchange header 110, as indicated by directional arrow 124, and from heat exchange header 110 through microchannel reactor core 101 to heat exchange footer 112, and out of heat exchange footer 112, as indicated by directional arrow 126. The reactants may be preheated prior to entering the

reactor zone. The hydrocarbon reactant and the oxygen or source of oxygen may be mixed prior to entering the reactor zone, or they may be mixed in the reactor zone.

5 Within the microchannel reactor core 101, the oxygen or source of oxygen may be added to the hydrocarbon reactant using staged addition. This is shown in Fig. 2 which illustrates repeating unit 130, which is used in the microchannel reactor 100 illustrated in Fig. 1. Repeating unit 130 is housed within housing unit 131 and includes process microchannels 140 and 150, oxidant microchannel 160, orifices 170, and heat exchange microchannels 180 and 190. The hydrocarbon reactant
10 flows through process microchannels 140 and 150, as indicated by the directional arrows 141 and 151, respectively. Oxygen or a source of oxygen flows through oxidant microchannel 160 into orifices 170, as indicated by directional arrows 161. The oxygen or oxygen source mixes with the hydrocarbon reactant in the process microchannels 140 and 150. The process microchannels 140 and 150 have
15 reaction zones 142 and 152, respectively, wherein the catalyst is present and the reactants contact the catalyst and undergo reaction to form the desired product, and channel zones 143 and 153, respectively, wherein further contact with the foregoing catalyst or a different catalyst may be effected, or product cooling and/or quenching may be effected. The catalyst positioned in the reaction zone is a partial oxidation
20 catalyst. In one embodiment, a combustion catalyst may be positioned downstream of the partial oxidation catalyst in the reaction zones 142 and 152 and/or in the channel zones 143 and 153. The product exits the process microchannels 140 and 150, as indicated by the directional arrows 144 and 154, respectively. The product exiting the process microchannels 140 and 150 flows to the manifold and
25 recuperator 108, and from the manifold and recuperator 108 through the product footer 106 as indicated by directional arrow 120. Heat exchange fluid flows from header 110 through heat exchange channels 180 and 190, as indicated by directional arrows 181, and 191 and 192, respectively, to heat exchange footer 112. The heat exchange channels 180 and 190 are aligned to provide a flow in a cross-
30 current direction relative to the process microchannels 140 and 150 as indicated by arrows 181, 191 and 192. The process microchannels 140 and 150 transfer heat to the heat exchange channels. The heat exchange fluid may be recirculated using known techniques. Alternatively, the heat exchange channels may be oriented to

provide for flow of the heat exchange fluid in a cocurrent or counter current direction relative to the direction of the flow of fluid through the process microchannels 140 and 150. The repeating unit 130 illustrated in Fig. 2 may occur once within the microchannel reactor 100 or it may be repeated any number of times, for example, two, three, four, five, ten, twenty, fifty, one hundred, hundreds, one thousand, thousands, ten thousand, tens of thousands, one hundred thousand, hundreds of thousands or millions of times. The staged oxygen addition provided for in this process provides the advantage of lowering local oxygen pressure and favoring desired lower-order partial oxidation reactions over higher-order competing and undesired combustion reactions.

Each of the process microchannels 140 and 150 and the oxidant microchannel 160 may have at least one internal dimension of height or width of up to about 10 mm, and in one embodiment from about 0.05 to about 10 mm, and in one embodiment about 0.05 to about 5 mm, and in one embodiment about 0.05 to about 2 mm, and in one embodiment about 0.05 to about 1.5 mm, and in one embodiment about 0.05 to about 1 mm, and in one embodiment about 0.05 to about 0.5 mm. The other internal dimension of height or width may be of any value, for example, it may range from about 0.1 cm to about 100 cm, and in one embodiment from about 0.1 to about 75 cm, and in one embodiment from about 0.1 to about 50 cm, and in one embodiment about 0.2 cm to about 25 cm. The length of each of the process microchannels 140 and 250, and the oxidant microchannel 160, may be of any value, for example, the lengths may range from about 1 cm to about 500 cm, and in one embodiment 1 cm to about 250 cm, and in one embodiment 1 cm to about 100 cm, and in one embodiment 1 cm to about 50 cm, and in one embodiment about 2 to about 25 cm.

Each of the heat exchange channels 180 and 190 may have at least one internal dimension of height or width of up to about 10 mm, and in one embodiment about 0.05 to about 10 mm, and in one embodiment about 0.05 to about 5 mm, and in one embodiment from about 0.05 to about 2 mm, and in one embodiment from about 0.5 to about 1 mm. The other internal dimension may range from about 1 mm to about 1 m, and in one embodiment about 1 mm to about 0.5 m, and in one embodiment about 2 mm to about 10 cm. The length of the heat exchange channels may range from about 1 mm to about 1 m, and in one embodiment about

1 cm to about 0.5 m. These heat exchange channels may be microchannels. The separation between each process microchannel 140 or 150 and the next adjacent heat exchange channel 180 or 190 may range from about 0.05 mm to about 5 mm, and in one embodiment about 0.2 mm to about 2 mm.

5 The microchannel reactor 100 may be made using known techniques. These include laminating interleaved shims, where shims designed for the process microchannels, oxidant microchannels and heat exchange channels are interleaved.

 The housing 131, process microchannels 140 and 150, oxidant microchannel 160, and heat exchange channels 180 and 190 may be made of any material that provides
10 sufficient strength, dimensional stability and heat transfer characteristics to permit operation of the inventive process. These materials include steel (e.g., stainless steel, carbon steel, and the like); monel; inconel; aluminum; titanium; nickel; platinum; rhodium; copper; chromium; brass; alloys of any of the foregoing metals; polymers (e.g., thermoset resins); ceramics; glass; composites comprising one or more polymers (e.g., thermoset resins) and
15 fiberglass; quartz; silicon; or a combination of two or more thereof.

 Alternatively, the staged addition of the oxygen or source of oxygen to the microchannel reactor may be effected using separate devices, through the use of small orifices or jets within one device, or from a microporous membrane or alternate sparging sheet. The staged addition of oxygen to partial oxidation reactions, and specifically oxidative
20 dehydrogenation reactions, is disclosed in Tonkovich, Zilka, Jimenz, Roberts, and Cox, 1996, "Experimental Investigations of Inorganic Membrane Reactors: a Distributed Feed Approach for Partial Oxidation Reactions," Chemical Engineering Science, 51 (5), 789-806).

 In one embodiment, the process microchannels 140 and 150 may contain a bulk flow path. The term "bulk flow path" refers to an open path (contiguous bulk flow region) within
25 the process microchannels. A contiguous bulk flow region allows rapid fluid flow through the microchannels without large pressure drops. In one embodiment, the flow of fluid in the bulk flow region is laminar. Bulk flow regions within each process microchannel may have a cross-sectional area of about 0.05 to about 10,000 mm², and in one embodiment about 0.05 to about 5000 mm², and in one embodiment about 0.1 to about 2500 mm², and in one
30 embodiment about 0.2

to about 1000 mm², and in one embodiment about 0.3 to about 500 mm², and in one embodiment about 0.4 to about 250 mm², and in one embodiment about 0.5 to about 125 mm². The bulk flow regions may comprise from about 5% to about 95%, and in one embodiment about 30% to about 80% of the cross-section of the process microchannels 140 and 150.

The reactant composition may be in the form of a fluid. This fluid may be a liquid or a gas, and in one embodiment it is in the form of a gas. This fluid may be in the form of a gas containing dispersed liquid droplets. The reactant composition comprises methane and may further comprise one or more additional hydrocarbon reactants. The concentration of methane in the mixture of methane and one or more additional hydrocarbon reactants may range up to about 100% methane, and in one embodiment from about 10 to about 90% by volume methane, and in one embodiment about 50 to about 90% by volume methane.

The purity of the reactant composition is not critical, though it is desirable to avoid the presence of compounds which may poison the catalyst. As a result, the reactant composition may further comprise impurities such as air, carbon dioxide, and the like.

The reactant composition may include a diluent material. Examples of such diluents include nitrogen, helium, carbon dioxide, liquid water, steam, and the like. The volume ratio of diluent to hydrocarbon reactant in the reactant composition may range from zero to about 80% by volume, and in one embodiment from zero to about 50% by volume. However, an advantage of at least one embodiment of the invention is that it is possible to conduct the inventive process without the use of such diluents, thus a more efficient and compact process may be provided.

The hydrocarbon reactant comprises methane and may further comprise one or more additional hydrocarbon compounds that are capable of undergoing an oxidation reaction, and are a fluid (and in one embodiment a vapor) at the temperature and pressure used within the process microchannels. Examples include saturated aliphatic compounds (e.g., alkanes), unsaturated aliphatic compounds (e.g., monoenes, polyenes, and the like), alkyl substituted aromatic compounds, alkylene substituted aromatic compounds, oils, normally liquid fuels, and the like.

The saturated aliphatic compounds include alkanes containing 2 to about 20 carbon atoms per molecule, and in one embodiment 2 to about 18 carbon atoms, and in one embodiment 2 to about 16 carbon atoms, and in one embodiment 2 to about 14 carbon atoms, and in one embodiment 2 to about 12 carbon atoms, and in one embodiment 2 to about 10 carbon atoms, and in one embodiment 2 to about 8 carbon atoms, and in one embodiment 2 to about 6 carbon atoms, and in one embodiment 2 to about 4 carbon atoms. These include ethane, propane, isopropane, butane, isobutane, the pentanes, the hexanes, the heptanes, the octanes, the nonanes, the decanes, and the like.

The unsaturated aliphatic compounds include alkenes or alkylenes containing 2 to about 20 carbon atoms, and in one embodiment 2 to about 18 carbon atoms, and in one embodiment 2 to about 16 carbon atoms, and in one embodiment 2 to about 14 carbon atoms, and in one embodiment 2 to about 12 carbon atoms, and in one embodiment 2 to about 10 carbon atoms, and in one embodiment 2 to about 8 carbon atoms, and in one embodiment 2 to about 6 carbon atoms per molecule, and in one embodiment 2 to about 4 carbon atoms. These include ethylene; propylene; 1-butene; 2-butene; isobutylene; 1-pentene; 2-pentene; 3-methyl-1-butene; 2-methyl-2-butene; 1-hexene; 2,3-dimethyl-2-butene; 1-heptene; 1-octene; 1-nonene; 1-decene; and the like.

The unsaturated aliphatic compounds may comprise polyenes. These include dienes, trienes, and the like. These compounds may contain 3 to about 20 carbon atoms per molecule, and in one embodiment 3 to about 18 carbon atoms, and in one embodiment 3 to about 16 carbon atoms, and in one embodiment 3 to about 14 carbon atoms, and in one embodiment 3 to about 12 carbon atoms, and in one embodiment 3 to about 10 carbon atoms, and in one embodiment about 4 to about 8 carbon atoms, and in one embodiment about 4 to about 6 carbon atoms. Examples include 1,2-propadiene (also known as allene); 1,3-butadiene; 2-methyl-1,3-butadiene (also known as isoprene); 1,3-pentadiene; 1,4-pentadiene; 1,5-hexadiene; 2,4-hexadiene; 2,3-dimethyl-1,3-butadiene; and the like.

The alkyl or alkylene substituted aromatic compounds may contain one or more alkyl or alkylene substituents. These compounds may be monocyclic (e.g., phenyl) or a polycyclic (e.g., naphthyl). These compounds include alkyl substituted aromatic compounds containing one or more alkyl groups containing 1 to about 20

carbon atoms, and in one embodiment 1 to about 18 carbon atoms, and in one
embodiment 1 to about 16 carbon atoms, and in one embodiment 1 to about 14
carbon atoms, and in one embodiment 1 to about 12 carbon atoms, and in one
embodiment 1 to about 10 carbon atoms, and in one embodiment 1 to about 8
5 carbon atoms, and in one embodiment about 2 to about 6 carbon atoms, and in one
embodiment about 2 to about 4 carbon atoms. These also include the alkylene
substituted aromatic compounds containing one or more alkylene groups containing
2 to about 20 carbon atoms, and in one embodiment 2 to about 18 carbon atoms,
and in one embodiment 2 to about 16 carbon atoms, and in one embodiment 2 to
10 about 14 carbon atoms, and in one embodiment 2 to about 12 carbon atoms, and
in one embodiment 2 to about 10 carbon atoms, and in one embodiment 2 to about
8 carbon atoms, and in one embodiment about 2 to about 6 carbon atoms, and in
one embodiment about 2 to about 4 carbon atoms. Examples include toluene, o-
xylene, m-xylene, p-xylene, hemimellitene, pseudocumene, mesitylene, prehnitene,
15 isodurene, durene, pentamethylbenzene, hexamethylbenzene, ethylbenzene, n-
propylbenzene, cumene, n-butylbenzene, isobutylbenzene, sec-butylbenzene, tert-
butylbenzene, p-cymene, styrene, and the like.

The hydrocarbon reactant may further comprise a natural oil, synthetic oil or
mixture thereof. The natural oils include animal oils and vegetable oils (e.g., castor
20 oil, lard oil) as well as mineral oils such as liquid petroleum oils. Oils derived from
coal or shale may be used. Synthetic oils include hydrocarbon oils such as
polymerized and interpolymerized olefins, polyphenyls, alkylated diphenyl esters,
alkylated diphenyl sulfides, and the like. Alkylene oxide polymers and interpolymers
and derivatives thereof where the thermal hydroxyl groups have been modified by
25 esterification, etherification, etc., constitute another class of known synthetic oils that
can be used as the hydrocarbon reactant. The synthetic oils that are useful as the
hydrocarbon reactant include the esters of dicarboxylic acids with a variety of
alcohols. The hydrocarbon reactant may comprise a poly-alpha-olefin. The
hydrocarbon reactant may comprise a Fischer-Tropsch synthesized hydrocarbon.
30 The hydrocarbon reactant may be obtained from a process stream generated during
oil refining, chemical synthesis, and the like.

The hydrocarbon reactant may further comprise a normally liquid
hydrocarbon fuel. These include distillate fuels such as motor gasoline, diesel fuel

or fuel oil. Hydrocarbon reactants derived from vegetable sources, mineral sources, and mixtures thereof may be used. These include hydrocarbon reactants derived from soybean, rapeseed, palm, shale, coal, tar sands, and the like.

5 The oxygen or oxygen source may comprise molecular oxygen, air or other oxidants, such as nitrogen oxides, which can function as a source of oxygen. The oxygen source may be carbon dioxide, carbon monoxide or a peroxide (e.g., hydrogen peroxide). Gaseous mixtures containing oxygen, such as mixtures of oxygen and air, or mixtures of oxygen and an inert gas (e.g., helium, argon, etc.) or a diluent gas (e.g., carbon dioxide, water vapor, etc.) may be used.

10 The mole ratio of carbon in the hydrocarbon reactant to oxygen may range from about 10:1 to about 1:1, and in one embodiment about 4:1 to about 1:1, and in one embodiment about 2.4:1 to about 1.6:1.

The heat exchange fluid may be any fluid. These include air, steam, liquid water, gaseous nitrogen, liquid nitrogen, other gases including inert gases, carbon monoxide, 15 molten salt, oils such as mineral oil, and heat exchange fluids such as Dowtherm A and Therminol which are available from Dow-Union Carbide.

The heat exchange fluid may comprise one or more of the reactant streams. This can provide process pre-heat and increase overall thermal efficiency of the process.

20 In one embodiment, the heat exchange channels comprise process channels wherein an endothermic reaction is conducted. These heat exchange process channels may be microchannels. Examples of endothermic reactions that may be conducted in the heat exchange channels include steam reforming and dehydrogenation reactions. A typical heat flux for convective cooling in a microchannel reactor is on the order of about 25 1 to about 10 W/cm². The incorporation of a simultaneous endothermic reaction to provide an improved heat sink may enable a typical heat flux of roughly an order of magnitude above the convective cooling heat flux. The use of simultaneous exothermic and endothermic reactions to exchange heat in a microchannel reactor is disclosed in U.S. Patent Application Serial No. 10/222,196, filed August 15, 2002.

30 In one embodiment, the heat exchange fluid undergoes a phase change as it flows through the heat exchange channels. This phase change provides

additional heat removal from the process microchannels beyond that provided by convective cooling. For a liquid heat exchange fluid being vaporized, the additional heat being transferred from the process microchannels would result from the latent heat of vaporization required by the heat exchange fluid. An example of such a phase change would be an oil or water that undergoes boiling.

The cooling of the process microchannels 140 and 150 during the inventive process, in one embodiment, is advantageous for controlling selectivity towards the main or desired product due to the fact that such added cooling reduces or eliminates the formation of undesired by-products from undesired parallel reactions with higher activation energies. As a result of this cooling, in one embodiment, the temperature of the reactant composition at the entrance to the process microchannels 140 and 150 may be within about 200°C, and in one embodiment within about 150°C, and in one embodiment within about 100°C, and in one embodiment within about 50°C, and in one embodiment within about 25°C, and in one embodiment within about 10°C, of the temperature of the product (or mixture of product and unreacted reactants) at the exit of the process microchannels.

The catalyst used in a microchannel reactor may have any size and geometric configuration that fits within the process microchannels. The catalyst may be in the form of particulate solids (e.g., pellets, powder, fibers, and the like) having a median particle diameter of about 1 to about 1000 µm, and in one embodiment about 10 to about 500 µm, and in one embodiment about 25 to about 250 µm. The catalyst may be supported in a porous structure such as a foam, felt, wad or a combination thereof. The term "foam" is used herein to refer to a structure with continuous walls defining pores throughout the structure. The term "felt" is used herein to refer to a structure of fibers with interstitial spaces therebetween. The term "wad" is used herein to refer to a structure of tangled strands, like steel wool. The catalyst may be supported on a honeycomb structure.

The catalyst may be in the form of a flow-by structure such as a felt with an adjacent gap, a foam with an adjacent gap, a fin structure with gaps, a washcoat on any inserted substrate, or a gauze that is parallel to the flow direction with a corresponding gap for flow. An example of a flow-by structure is illustrated in Fig. 3. In Fig. 3, the catalyst 300 is contained within process microchannel 302. An open

passage way 304 permits the flow of fluid through the process microchannel 302 in contact with the catalyst 300 as indicated by arrows 306 and 308.

5 The catalyst may be in the form of a flow-through structure such as a foam, wad, pellet, powder, or gauze. An example of a flow-through structure is illustrated in Fig. 4. In Fig. 4, the flow-through catalyst 400 is contained within process microchannel 402 and the fluid flows through the catalyst 400 as indicated by arrows 404 and 406.

10 The catalyst may be directly washcoated on the interior walls of the process microchannels, grown on the walls from solution, or coated in situ on a fin structure. The catalyst may be in the form of a single piece of porous contiguous material, or many pieces in physical contact. In one embodiment, the catalyst is comprised of a contiguous material and has a contiguous porosity such that molecules can diffuse through the catalyst. In this embodiment, the fluids flow through the catalyst rather than around it. In one embodiment, the cross-sectional area of the catalyst occupies about 1 to about 99%, and in one embodiment about 10 to about 95% of the cross-sectional area of the process microchannels. The catalyst may have a surface area, as measured by BET, of greater than about 0.5 m²/g, and in one embodiment greater than about 2 m²/g.

20 The catalyst may comprise a porous support, an interfacial layer on the porous support, and a catalyst material on the interfacial layer. The interfacial layer may be solution deposited on the support or it may be deposited by chemical vapor deposition or physical vapor deposition. In one embodiment the catalyst has a porous support, a buffer layer, an interfacial layer, and a catalyst material. Any of the foregoing layers may be continuous or discontinuous as in the form of spots or dots, or in the form of a layer with gaps or holes.

25 The porous support may have a porosity of at least about 5% as measured by mercury porosimetry and an average pore size (sum of pore diameters divided by number of pores) of about 1 to about 1000 μm. The porous support may be a porous ceramic or a metal foam. Other porous supports that may be used include carbides, nitrides, and composite materials. The porous support may have a porosity of about 30% to about 99%, and in one embodiment about 60% to about 98%. The porous support may be in the form of a foam, felt, wad, or a combination thereof. The open cells of the metal foam may range from about 20 pores per inch

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(ppi) to about 3000 ppi, and in one embodiment about 20 to about 1000 ppi, and in one embodiment about 40 to about 120 ppi. The term "ppi" refers to the largest number of pores per inch (in isotropic materials the direction of the measurement is irrelevant; however, in anisotropic materials, the measurement is done in the direction that maximizes pore number).

The buffer layer, when present, may have a different composition and/or density than both the porous support and the interfacial layers, and in one embodiment has a coefficient of thermal expansion that is intermediate the thermal expansion coefficients of the porous support and the interfacial layer. The buffer layer may be a metal oxide or metal carbide. The buffer layer may be comprised of Al_2O_3 , TiO_2 , SiO_2 , ZrO_2 , or combination thereof. The Al_2O_3 may be α - Al_2O_3 , γ - Al_2O_3 or a combination thereof. α - Al_2O_3 provides the advantage of excellent resistance to oxygen diffusion. The buffer layer may be formed of two or more compositionally different sublayers. For example, when the porous support is metal, for example a stainless steel foam, a buffer layer formed of two compositionally different sub-layers may be used. The first sublayer (in contact with the porous support) may be TiO_2 . The second sublayer may be α - Al_2O_3 which is placed upon the TiO_2 . In one embodiment, the α - Al_2O_3 sublayer is a dense layer that provides protection of the underlying metal surface. A less dense, high surface area interfacial layer such as alumina may then be deposited as support for a catalytically active layer.

The porous support may have a thermal coefficient of expansion different from that of the interfacial layer. In such a case a buffer layer may be needed to transition between the two coefficients of thermal expansion. The thermal expansion coefficient of the buffer layer can be tailored by controlling its composition to obtain an expansion coefficient that is compatible with the expansion coefficients of the porous support and interfacial layers. The buffer layer should be free of openings and pin holes to provide superior protection of the underlying support. The buffer layer may be nonporous. The buffer layer may have a thickness that is less than one half of the average pore size of the porous support. The buffer layer may have a thickness of about 0.05 to about 10 μm , and in one embodiment about 0.05 to about 5 μm .

In one embodiment of the invention, adequate adhesion and chemical stability may be obtained without a buffer layer. In this embodiment the buffer layer may be omitted.

5 The interfacial layer may comprise nitrides, carbides, sulfides, halides, metal oxides, carbon, or a combination thereof. The interfacial layer provides high surface area and/or provides a desirable catalyst-support interaction for supported catalysts. The interfacial layer may be comprised of any material that is conventionally used as a catalyst support. The interfacial layer may be comprised of a metal oxide. Examples of metal oxides that may be used include γ -Al₂O₃, SiO₂, ZrO₂, TiO₂,
10 tungsten oxide, magnesium oxide, vanadium oxide, chromium oxide, manganese oxide, iron oxide, nickel oxide, cobalt oxide, copper oxide, zinc oxide, molybdenum oxide, tin oxide, calcium oxide, aluminum oxide, lanthanum series oxide(s), zeolite(s) and combinations thereof. The interfacial layer may serve as a catalytically active layer without any further catalytically active material deposited thereon. Usually, however, the interfacial layer is used in combination with a catalytically active layer. The interfacial layer may also be formed of two or more compositionally different sublayers. The interfacial layer may have a thickness that is less than one half of the average pore size of the porous support. The interfacial layer thickness may range from about 0.5 to about 100 μ m, and in one embodiment
15 from about 1 to about 50 μ m. The interfacial layer may be either crystalline or amorphous. The interfacial layer may have a BET surface area of at least about 1 m²/g.

The catalyst may be deposited on the interfacial layer. Alternatively, the catalyst material may be simultaneously deposited with the interfacial layer. The catalyst layer may be intimately dispersed on the interfacial layer. That the catalyst layer is "dispersed on" or "deposited on" the interfacial layer includes the
25 conventional understanding that microscopic catalyst particles are dispersed: on the support layer (i. e., interfacial layer) surface, in crevices in the support layer, and in open pores in the support layer.

30 The catalyst may be supported on an assembly of one or more fins which may be positioned within each of the process microchannels. Examples are illustrated in Figs. 5-7. Referring to Fig. 5, fin assembly 500 includes fins 502 which are mounted on fin support 504 which overlies base wall 506 of process

microchannel 508. The fins 502 project from the fin support 504 into the interior of the process microchannel 508. The fins 502 extend to and contact the interior surface of upper wall 510 of process microchannel 508. The fin channels 512 between the fins 502 provide passage ways for fluid to flow through the process microchannel 508 parallel to its length. Each of the fins 502 has an exterior surface on each of its sides, this exterior surface provides a support base for a catalyst. With the inventive process, the reactant composition flows through the fin channels 512, contact the catalyst supported on the exterior surface of the fins 502, and react to form a product. The fin assembly 500a illustrated in Fig. 6 is similar to the fin assembly 500 illustrated in Fig. 5 except that the fins 502a do not extend all the way to the interior surface of the upper wall 510 of the microchannel 508. The fin assembly 500b illustrated in Fig. 7 is similar to the fin assembly 500 illustrated in Fig. 5 except that the fins 502b in the fin assembly 500b have cross sectional shapes in the form of trapezoids. Each of the fins may have a height ranging from about 0.02 mm up to the height of the process microchannel 508, and in one embodiment from about 0.02 to about 10 mm, and in one embodiment from about 0.02 to about 5 mm, and in one embodiment from about 0.02 to about 2 mm. The width of each fin may range from about 0.02 to about 5 mm, and in one embodiment from about 0.02 to about 2 mm and in one embodiment about 0.02 to about 1 mm. The length of each fin may be of any length up to the length of the process microchannel 508, and in one embodiment from about 5 mm to about 500 cm, and in one embodiment about 1 cm to about 250 cm, and in one embodiment about 1 cm to about 100 cm, and in one embodiment about 2 cm to about 25 cm. The gap between each of the fins may be of any value and may range from about 0.02 to about 5 mm, and in one embodiment from about 0.02 to about 2 mm, and in one embodiment from about 0.02 to about 1 mm. The number of fins in the process microchannel 508 may range from about 1 to about 50 fins per centimeter of width of the process microchannel 508, and in one embodiment from about 1 to about 30 fins per centimeter, and in one embodiment from about 1 to about 10 fins per centimeter, and in one embodiment from about 1 to about 5 fins per centimeter, and in one embodiment from about 1 to about 3 fins per centimeter. Each of the fins may have a cross-section in the form of a rectangle or square as illustrated in Figs. 5 and 6, or a trapezoid as illustrated in Fig. 7. When viewed along its length, each fin may

be straight, tapered or have a serpentine configuration. The fins may be made of any material that provides sufficient strength, dimensional stability and heat transfer characteristics to permit operation for which the process microchannel is intended.

These materials include: steel (e.g., stainless steel, carbon steel, and the like); monel; 5 inconel; aluminum; titanium; nickel; platinum; rhodium; copper; chromium; brass; alloys of any of the foregoing metals; polymers (e.g., thermoset resins); ceramics; glass; composites comprising one or more polymers (e.g., thermoset resins) and fiberglass; quartz; silicon; or a combination of two or more thereof. The fin may be made of an Al_2O_3 forming material such as an alloy comprising Fe, Cr, Al and Y, or a Cr_2O_3 forming 10 material such as an alloy of Ni, Cr and Fe.

The catalyst may comprise Rh, Pt, Ni, Cr, Ru, Pd, Os, Ir, or an oxide thereof, or a mixture of two or more thereof. Partial oxidation catalysts based on one or more of the foregoing are disclosed in U.S. Patents 5,648,582 and 6,409,940 B1; U.S. Patent Application Publications 2002/0004450 A1, 2002/0012624 A1 and 2002/0115730 A1; 15 PCT International Publication Nos. WO 99/48805, WO 01/80992 A2 and WO 02/066403 A1; and European Patent Application Publication Nos. EP 0640561 A1, EP 0725038 A1 and EP 0741107 A1. These catalysts may be in any of the forms or supported on any of the support structures discussed above.

The partial oxidation catalyst may comprise platinum or an oxide thereof 20 deposited on a ceramic support as disclosed in U.S. Patent 5,648,582.

The partial oxidation catalyst may comprise nickel and rhodium, or oxides thereof, deposited on a support structure made of a spinel, a perovskite, magnesium oxide, a pyrochlore, a brownmillerite, zirconium phosphate, magnesium stabilized zirconia, zirconia stabilized alumina, silicon carbide, yttrium stabilized zirconia, calcium 25 stabilized zirconia, yttrium aluminum garnet, alumina, cordierite, ZrO_2 , MgAl_2O_4 , SiO_2 or TiO_2 . These are disclosed in U.S. Patent 6,409,940 B1.

The partial oxidation catalyst may comprise a lanthanide-promoted rhodium catalyst as disclosed in U.S. Patent Publication No. 2002/0115730 A1.

The partial oxidation catalyst may comprise a Ni-Cr, Ni-Co-Cr or Ni-Rh alloy as 30 disclosed in U.S. Patent Publication No. 2002/0012624 A1.

The partial oxidation catalyst may comprise rhodium, nickel, chromium, or a combination thereof supported on ceramic oxide fiber as disclosed in U. S. Patent Publication No. 2002/0004450 A1.

5 The partial oxidation catalyst may comprise rhodium supported on a refractory oxide support as disclosed in PCT International Publication No. WO 99/48805.

The partial oxidation catalyst may comprise a rhodium gauze or rhodium felt as disclosed in PCT International Publication No. WO 01/80992 A2.

The partial oxidation catalyst may comprise a rhodium-spinel catalyst as disclosed in PCT International Publication No. WO 02/066403 A1.

10 The partial oxidation catalyst may comprise a Group VIII metal (e.g., Ru, Rh, Pd, Os, Ir, Pt) supported on a refractory oxide having at least two cations as disclosed in EP 0640561 A1.

The partial oxidation catalyst may comprise rhodium and/or ruthenium having a layered hydrotalcite type structure as disclosed in EP 0725038 A1.

15 The partial oxidation catalyst may comprise a nickel-based catalyst or ruthenium based catalyst as disclosed in EP 0741107 A2.

The partial oxidation catalyst may comprise a composition represented by the formula



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wherein in formula (I): M^1 is Rh, Ni, Pd, Pt, Ru, Co or a mixture of two or more thereof; M^2 is Ce, Pr, Tb or a mixture of two or more thereof; M^3 is La, Ba, Zr, Mg, Ca or a mixture of two or more thereof; a is a number in the range of about 0.0001 to about 1, and in one embodiment 0.01 to about 1; b is a number in the range of zero to about
25 0.9999, and in one embodiment zero to about 0.2; c is a number in the range of about 0.0001 to about 0.9999, and in one embodiment about 0.01 to about

0.2; d is a number in the range of about 0.0001 to about 0.9999, and in one embodiment about 0.1 to about 0.9; and x is the number of oxygens needed to fulfill the valency requirements of the elements present; the catalyst being coated on a substrate or supported on a foam, felt, wad or fin. In one embodiment M^1 is Rh or Ni, and in one embodiment it is Rh. In one embodiment M^3 is La or Mg, and in one embodiment it is La. In one embodiment the catalyst may be represented by the formula $Rh/LaAl_{11}O_{18}$ or $Rh/LaAlO_3$.

In one embodiment, the process for making the catalyst represented by formula (I) comprises the steps of: (A) applying a layer of Al_2O_3 over the native oxide layer to form a treated support structure; (B) calcining the treated support structure formed in step (A); (C) applying a promoter or stabilizer to the surface of the calcined support structure formed in step (B), the promoter or stabilizer comprising La, Ba, Zr, Mg, Ca, or an oxide or nitrate thereof, or a mixture of two or more thereof; (D) calcining the treated support structure formed in step (C); (E) applying a catalytic metal, or oxide or nitrate thereof, to the surface of the calcined support structure formed in step (D), the catalytic metal comprising Rh, Ni, Pd, Pt, Ru, Co, or a mixture of two or more thereof; and (F) calcining the treated support structure formed in step (F) to form the supported catalyst. In one embodiment, the catalyst formed in step (F) may be reduced in hydrogen.

The support structure may be made of a material comprising: steel; aluminum; titanium; iron; nickel; platinum; rhodium; copper; chromium; brass; an alloy of any of the foregoing metals; a polymer; ceramics; glass; a composite comprising polymer and fiberglass; quartz; silicon; or a combination of two or more thereof. In one embodiment the support structure may be made of an alloy comprising Fe, Cr, Al and Y, and the native oxide layer may comprise Al_2O_3 . In one embodiment, the support structure may be made of an alloy comprising Ni, Cr and Fe, and the native oxide layer may comprise Cr_2O_3 . In one embodiment, the promoter or stabilizer may be La or Mg, and in one embodiment it is La. In one embodiment, the catalytic metal is Rh or Ni, and in one embodiment it is Rh.

The support structure may be heated prior to step (A) to a temperature in the range of about 300°C to about 1400°C, and in one embodiment about 700 to about 1200°C, for about 0.1 to about 1000 hours, and in one embodiment about 1 to about 10 hours. When the support structure is made of metal, this heat treating step

advantageously provides a layer of native oxide on the surface of the support structure.

During step (A) a slurry comprising Al_2O_3 or a colloidal dispersion (i.e., a sol) comprising Al_2O_3 may be applied over the native oxide layer. The slurry may
5 comprise about 1 to about 50% by weight Al_2O_3 , up to about 20% by weight ZrO_2 , up to about 25% by weight $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, with the remainder being water. The slurry coating may have a thickness of about 10 to about 100 microns. The colloidal dispersion may contain about 1% to about 30% by weight Al_2O_3 with the remainder being water. The colloidal dispersion coating may have a thickness of about 1 to
10 about 50 microns.

During step (B) the treated support structure may be calcined in air at a temperature in the range of about 150°C to about 1200°C , and in one embodiment about 300 to about 700°C , for about 0.1 to about 1000 hours, and in one embodiment about 1 to about 10 hours.

During step (C) a solution comprising $\text{La}(\text{NO}_3)_3$ may be applied to the surface of the calcined support structure.
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During step (D) the treated support structure may be calcined in air at a temperature in the range of about 150°C to about 1200°C , and in one embodiment about 500 to about 1100°C , for about 0.1 to about 1000 hours, and in one
20 embodiment about 1 to about 10 hours.

During step (E) a composition comprising $\text{Rh}(\text{NO}_3)_3$ may be applied to the surface of the calcined support structure.

During step (F) the treated support structure may be calcined in air at a temperature in the range of about 150°C to about 1200°C , and in one embodiment about 400°C to about 1100°C , for about 0.1 to about 1000 hours, and in one
25 embodiment about 1 to about 10 hours.

The combustion catalyst may comprise any combustion catalyst. These include, for example, noble metals such as Pt, Rh, Pd, Co, Cu, Mn, Fe, Ni; oxides of any of these metals; perovskites and aluminates. In one embodiment, the
30 combustion catalyst is accompanied by an activity-enhancing promoter such as Ce, Tb or Pr, their oxides, and combinations thereof. In one embodiment, a promoter element is present in at least about 1:1 molar ratio as compared to the active catalyst element or elements, and in one embodiment a promoter element is present

in the range of about 0.5:1 to about 10:1 molar ratio as compared to an active catalyst element (moles promoter(s): moles active catalyst element(s)). These catalysts may be in any of the forms or supported on any of the support structures discussed above.

5 The contact time of the reactants and/or products with the catalyst within the process microchannels may range up to about 500 milliseconds (ms), and in one embodiment from about 0.1 ms to about 500 ms, and in one embodiment about 0.1 ms to about 400 ms, and in one embodiment about 0.1 ms to about 300 ms, and in one embodiment about 0.1 ms to about 200 ms, and in one embodiment about 0.1 ms to about 100 ms, and in one embodiment from about 1 ms to about 75 ms, and in one embodiment about 1 ms to about 50 ms, and in one embodiment about 1 ms to about 25 ms, and in one embodiment about 1 ms to about 10 ms, and in one embodiment about 1 ms to about 5 ms.

15 The space velocity (or gas hourly space velocity) for the flow of the reactant composition and product through the process microchannels may be at least about 100 hr⁻¹ (normal liters of hydrocarbon/hour/liter of reaction chamber) or at least about 100 ml feed/(g catalyst) (hr). The space velocity may range from about 100 to about 2,000,000 hr⁻¹ based on the volume of the process microchannels, or from about 100 to about 2,000,000 ml feed/(g catalyst) (hr). In one embodiment, the space velocity may range from about 500 to about 1,000,000 hr⁻¹, or about 500 to about 1,000,000 ml feed/(g catalyst) (hr), and in one embodiment from about 1000 to about 1,000,000 hr⁻¹, or from about 1000 to about 1,000,000 ml feed/(g catalyst) (hr).

25 The temperature of the reactant composition entering the process microchannels may range from about 200°C to about 1000°C, and in one embodiment about 150°C to about 700°C, and in one embodiment about 150°C to about 600°C, and in one embodiment about 200°C to about 600°C. In one embodiment the temperature may be in the range of about 150°C to about 500°C, and in one embodiment about 150°C to about 400°C, and in one embodiment about 200°C to about 300°C. In one embodiment, the temperature may be in the range of about 335°C to about 1000°C.

30 The temperature of the reactant composition and product within the process microchannel may range up to about 1150°C, and in one embodiment up to about

1100°C, and in one embodiment up to about 1050°C, and in one embodiment up to about 1000°C, and in one embodiment up to about 950°C, and in one embodiment up to about 900°C, and in one embodiment up to about 850°C, and in one embodiment up to about 800°C, and in one embodiment up to about 750°C, and in one embodiment up to about 700°C.

The reactant composition entering the process microchannels may be at a pressure of at least about 0.1 atmosphere, and in one embodiment at least about 0.5 atmosphere. In one embodiment the pressure may range from about 0.1 to about 100 atmospheres, and in one embodiment from about 0.5 to about 50 atmospheres, and in one embodiment about 1 to about 40 atmospheres, and in one embodiment from about 1 to about 35 atmospheres.

The pressure drop of the reactants and/or products as they flow through the process microchannels may range up to about 2 atmospheres per meter of length of the process microchannel (atm/m), and in one embodiment up to about 1 atm/m, and in one embodiment up to about 0.5 atm/m, and in one embodiment up to about 0.2 atm/m.

The flow of the reactants and/or products through the process microchannels may be laminar or in transition, and in one embodiment it is laminar. The Reynolds Number for the flow of reactants and/or products through the process microchannels may be up to about 4000, and in one embodiment up to about 2300, and in one embodiment in the range of about 10 to about 2000, and in one embodiment about 100 to about 1500.

The heat exchange fluid entering the heat exchange channels may have a temperature of about -70°C to about 650°C, and in one embodiment about 0°C to about 500°C, and in one embodiment about 100°C to about 300°C. The heat exchange fluid exiting the heat exchange channels may have a temperature in the range of about -60°C to about 630°C, and in one embodiment about 10°C to about 490°C. The residence time of the heat exchange fluid in the heat exchange channels may range from about 1 to about 1000 ms, and in one embodiment about 1 to about 500 ms, and in one embodiment from 1 to about 100 ms. The pressure drop for the heat exchange fluid as it flows through the heat exchange channels may range from about 0.05 to about 50 psi/ft, and in one embodiment from about 1 to about 25 psi/ft. The flow of the heat exchange fluid through the heat exchange

channels may be laminar or in transition, and in one embodiment it is laminar. The Reynolds Number for the flow of heat exchange fluid flowing through the heat exchange channels may be up to about 4000, and in one embodiment up to about 2300, and in one embodiment in the range of about 10 to about 2000, and in one
5 embodiment about 10 to about 1500.

The product exiting the microchannel reactor may be at a temperature in the range of about 100°C to about 1000°C, and in one embodiment about 200°C to about 800°C, and in one embodiment about 300°C to about 600°C. The product may be cooled to a temperature in the range of about 50°C to about 300°C, and in
10 one embodiment about 50°C to about 200°C, and in one embodiment about 50°C to 150°C, and in one embodiment about 50°C to about 100°C, in about 5 to about 100 ms, and in one embodiment about 5 to about 75 ms, and in one embodiment about 5 to about 50 ms, and in one embodiment about 10 to about 50 ms.

Advantages of the inventive process include: maximization of contact
15 between the hydrocarbon reactant, oxygen or source of oxygen, and the catalyst; and minimization of undesired reactions.

Advantages of the inventive process include the possibility of process intensification. Conventional processes of the prior art often operate under conditions of reactant dilution to prevent runaway reactions, while the inventive
20 process may be operated, if desired, under more intensive conditions leading to greater throughput. By combining catalytic microchannel processing with heat exchange it is possible to operate at hydrocarbon feed/oxygen ratios that would conventionally lead to high temperatures and loss of selectivity, but by removing heat rapidly through heat exchange, the temperature in the process microchannels
25 may be maintained relatively low, for example, below about 700°C, and in one embodiment below about 600°C, and in one embodiment below about 500°C, thus maximizing selectivity to desired products.

Advantages of the inventive process include the enhancement of reaction selectivity due to the dimensions of the microchannel reactor. In reactors of
30 conventional dimension, reactions propagated homogeneously in the in the gaseous phase make a significant contribution to the overall make-up of the product. These reactions tend to be indiscriminate and often result in the production of undesirable by-products such as CO and CO₂ or hydrocarbon pyrolysis products. For example,

if the reactant mixture contains propane, full and partial oxidation can take place as well as pyrolysis leading to the production of ethane and methane.

5 The level of conversion of the hydrocarbon reactant may be about 50% or higher, and in one embodiment about 60% or higher, and in one embodiment about 70% or higher, and in one embodiment about 80% or higher.

10 The level of selectivity of the desired product may be about 30% or higher, and in one embodiment about 50% or higher, and in one embodiment about 60% or higher, and in one embodiment about 70% or higher, and in one embodiment about 80% or higher, and in one embodiment about 85% or higher, and in one embodiment about 90% or higher, and in one embodiment about 95% or higher. In one embodiment, the level of selectivity to the desired product may be in the range of about 50% to about 95% , and in one embodiment about 75% to about 95%.

15 The yield of the desired product may be about 9% or higher per cycle, and in one embodiment about 20% or higher, and in one embodiment about 40% or higher, and in one embodiment about 50% or higher per cycle, and in one embodiment about 70% or higher, and in one embodiment 80% or higher, and in one embodiment about 90% or higher per cycle. The term "cycle" is used herein to refer to a single pass of the reactants through the process microchannels.

20 In one embodiment, the level of conversion of the hydrocarbon reactant is at least about 30%, the level of selectivity of the desired product is at least about 30%, and the yield of the desired product is at least about 9% per cycle.

25 In one embodiment, the process is conducted in a reactor containing a plurality of heat exchange channels operating in parallel, the total pressure drop for the heat exchange fluid flowing through the heat exchange channels is up to about 10 atmospheres, and in one embodiment up to about 5 atmospheres, and in one embodiment up to about 2 atmospheres.

Example 1

30 La_2O_3 stabilized Al_2O_3 is synthesized by using a sol-gel technique as follows. 24.7 g of aluminum butoxide are dissolved into 74.5 g of 2-butanol in a beaker with constant stirring. In another beaker, 4.0 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ are dissolved into 59.7 g of ethanol with constant stirring. The two solutions are mixed and stirred for 15 min. Subsequently 4.4 g of deionized H_2O are added slowly into the mixture. The obtained solution is heated to 80-100°C and kept it at this temperature for 2 hours.

The alcohols are vaporized during this time. The resulting solid is dried at 120°C overnight and calcined at 1000°C for 24 hours in air at a heating and cooling rate of 4 °C/min. The resulting material has 22 wt.% La₂O₃ and 78 wt.% Al₂O₃. Its BET surface area and pore volume are 64 m²/g and 0.35 cm³/g, respectively. The solid is crushed and 88-150 microns particles are chosen as catalyst support.

Rh/La₂O₃-Al₂O₃ catalyst is prepared by incipient wetness impregnation as follows. 0.96 g of 10 wt.% Rh(NO₃)₃ solution are dropped onto 0.8 g of the La₂O₃-Al₂O₃ particles. After drying at 120°C for 1 hour, the sample is calcined at 500°C for 1 hour in air at a heating and cooling rate of 3.5°C/min. This impregnation process is repeated once. The catalyst is calcined at 800°C for 1 hour. The Rh loading is 8.0 wt.%.

30 mg of catalyst are loaded in a tube reactor for testing partial oxidation of methane activity. The catalyst is reduced with H₂ at 450°C for 30 min before use. The feed gas composition contains 29.6% of CH₄ and 70.4% of air (CH₄/O₂ = 2/1), with 3.4 standard liters per minute (SLPM). The gas hourly space velocity (GHSV) is 5.8 x 10⁶ h⁻¹. CH₄ conversion is calculated by the difference in methane flow rates before the reaction and after the reaction. CO selectivity is obtained by [CO]/([CO] + [CO₂]) and H₂ selectivity is calculated by [H₂]/([H₂] + [H₂O]). At a tube skin temperature of 700°C, 88% of CH₄ conversion, 97% of CO selectivity and 91% of H₂ selectivity are obtained. O₂ conversion is 100%.

Example 2

La₂O₃ stabilized Al₂O₃ was synthesized by a sol-gel technique as follows. 24.7 g of aluminum butoxide are dissolved into 74.5 g of 2-butanol in a beaker with stirring. In another beaker, 4.0 g of La(NO₃)₃•6H₂O are dissolved into 59.7 g of ethanol with stirring. The two solutions are mixed and stirred for 15 min. Subsequently 4.4 g of deionized H₂O are added slowly into the mixture. The obtained solution is heated to 80-100°C and maintained at this temperature for 2 hours. The alcohols are vaporized during this time. The resulting solid is dried at 120°C overnight and calcined at 1000°C for 24 hours in air at a heating and cooling rate of 4°C/min. The resulting material contains 22 wt.% La₂O₃ and 78 wt.% Al₂O₃. Its BET surface area and pore volume are 64 m²/g and 0.35 cm³/g, respectively. The solid is crushed and 88-150 microns particles are chosen as catalyst support.

Rh/La₂O₃-Al₂O₃ catalyst is prepared by incipient wetness impregnation as follows. 0.96 g of 10 wt.% Rh(NO₃)₃ solution are dropped onto 0.8 g of the La₂O₃-Al₂O₃ particles. After drying at 120°C for 1 hour, the sample is calcined at 500°C for 1 hour in air at a heating and cooling rate of 3.5°C/min. This impregnation process is repeated once. The catalyst is calcined at 1000°C for 1 hour. The Rh loading is 8.0 wt.%.

30 mg of catalyst are loaded in a tube reactor for testing partial oxidation of methane activity. The catalyst is reduced with H₂ at 450°C for 30 min before use. The feed gas compositions are 29.6% of CH₄ and 70.4% of air (CH₄/O₂ = 2/1), with 3.4 SLPM. GHSV is 5.8 x 10⁶ h⁻¹. The tube skin temperature is 700°C. 90% of CH₄ conversion, 97% of CO selectivity and 87% of H₂ selectivity are obtained. O₂ conversion is 100%. The process is conducted for 260 hours. The results are disclosed in Fig. 8.

These tests results indicate that this catalyst is very stable. As shown in Fig. 8, CH₄ conversion, CO selectivity and H₂ selectivity are substantially unchanged during 260 hours time-on-stream. These results demonstrate that the Rh/La₂O₃-Al₂O₃ catalyst is highly active for the partial oxidation of methane to CO and H₂ at an extremely high space velocity.

Example 3

Fig. 7 shows the geometry of a fin that is useful for conducting a partial oxidation reaction process in a process microchannel. The trapezoidal shape of the fins provides mechanical rigidity at the base of fins. All the fins are supported on rectangular base to enhance heat transfer characteristics of the fin. The fin is fabricated from FeCrAlY using the Wire EDM method. The following table summarizes dimensions of the fin:

	Dimension (in)
Fin thickness	
At base	0.005
At top	0.002
Fin spacing	
At base	0.012
At top	0.017

Fin height	0.029
Rectangular base height	0.020
Overall width	0.180
Overall Height	0.049
Overall length	1.500

An Al_2O_3 slurry is prepared by mixing 7.2 g of gamma Al_2O_3 powder, 12 g of deionized H_2O and 42 g Al_2O_3 beads with 3 mm diameter. The pH value is adjusted to 3.5-4 using nitric acid. The Al_2O_3 is acidic gamma Al_2O_3 which is ground to powder smaller than 150 micrometers. The mixture is ball-milled for 8 hours. 0.8 g of 25 wt.% Al_2O_3 sol (Sasol 14N4-25) is added to 4.2 g of the slurry with stirring.

The FeCrAlY fin is cleaned in iso-propanol for 20 min with sonication. After drying at 100°C for 1 h and cooling to room temperature, the fin is cleaned in 20 wt.% HNO_3 solution for 20 min with sonication. The fin is then rinsed with deionized water until the pH value is 7. After drying at 120°C for 1 hour, the fin is heated to 1000°C in air at a heating rate of $3.5^\circ\text{C}/\text{min}$ and calcined at 1000°C for 8 hours in air. A dense Al_2O_3 layer is generated after the calcination. The Al_2O_3 layer functions as a protection scale and also improves the adhesion between the coating and the fin. The Al_2O_3 slurry is washcoated onto the fin by dipping. The excess slurry is removed by jetting air over the coated surface. The fin is dried at 120°C for 1 hour and then calcined at 450°C for 4 hours at a heating and cooling rate of $3.5^\circ\text{C}/\text{min}$. A 7.5 wt.% $\text{La}(\text{NO}_3)_3$ solution is impregnated onto the fin by dipping. The fin is dried at 120°C for 1 hour and then calcined at 1000°C for 4 hours in air at a heating and cooling rate of $3.5^\circ\text{C}/\text{min}$. The La_2O_3 on the surface stabilizes the Al_2O_3 . The slurry loading is 25.4 mg per fin. A 10 wt.% $\text{Rh}(\text{NO}_3)_3$ solution is dropped onto the fin and the excess solution is blown out by compressed air. The resulting fin supported catalyst is dried at 120°C for 1 hour and then calcined at 1000°C for 1 h in air. The Rh loading is 4.8 mg per fin.

The fin supported catalyst is tested for partial oxidation of methane to syngas at 1 atmosphere in a pellet. The pellet is a cylindrical metal rod having a diameter of 0.5 inch and a length of 2 inches. The pellet has a rectangular microchannel cut-

away in its center. The cut-away extends through the rod along its interior axis. The cut-away has a height of 0.05 inch and a width of 0.18 inch. The fin supported catalyst is placed in the cut-away for testing. Gas tight connections are made on each side of the cut-away. The reactants flow through tubing to the cut-away, and through the cut-away in contact with the fin supported catalyst. The pellet is placed in a furnace. The temperature of the furnace is increased to keep the pellet outside skin temperature at mid-length at 850°C. The temperature of the feed stream at the inlet of the furnace is at room temperature and is preheated before entering the pellet. The length of the tubing from the entrance of the furnace to the pellet is 10 feet. The outlet pressure of the product stream is atmospheric pressure. The pressure drop in the pellet is measured using a Capsuhelic differential pressure gauge. The composition of the product is analyzed with a two-column Gas Chromatograph. The performance of the fin supported catalyst is measured in terms of CH₄ conversion, H₂ selectivity and CO selectivity.

$$\text{CH}_4 \text{ Conversion (\%)} = (V_{\text{CH}_4, \text{ in}} - V_{\text{CH}_4, \text{ out}}) / (V_{\text{CH}_4, \text{ in}}) \times 100$$

$$\text{H}_2 \text{ Selectivity (\%)} = (V_{\text{H}_2, \text{ out, actual}}) / (V_{\text{H}_2, \text{ out, theoretical}}) \times 100$$

$$\text{CO Selectivity (\%)} = (V_{\text{CO, out}}) / (V_{\text{CO, out}} + V_{\text{CO}_2, \text{ out}}) \times 100$$

The catalyst is reduced with H₂ at 400°C for 30 min before use. The feed gas compositions are 29.6% of CH₄ and 70.4% of air (CH₄/O₂ = 2/1), with 2030 ml/min of total flow rate (standard conditions). The contact time is 3.3 ms. The contact time is defined as the ratio of flow volume in the pellet without the fin to the volumetric flow rate. The following table summarizes the fin supported catalyst performance after 157 hours of operation.

Parameter	Value
Coating Type	Powder slurry wash-coat
Fuel composition	29.6% CH ₄ , 70.4% air
Fuel contact time	3.3 ms
CH ₄ Conversion (at 850°C)	85%
H ₂ Selectivity (at 850°C)	92%
CO Selectivity (at 850°C)	95%

Pressure drop	5.6 psi
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Example 4

An alternate fin for use in a partial oxidation reaction process provides the advantage of reduced pressure drop. The flow area is increased by reducing number of fins. There are five fins projecting up from the fin support. The fins have a trapezoidal cross section as indicated in Fig. 7. The thickness of the fin along with trapezoidal shape of the fins provides mechanical rigidity at the base of the fins. The fins are supported on rectangular support or base to enhance heat transfer characteristics of the fin. The fin is made from FeCrAlY. The fin is fabricated by the wire EDM method. The following table summarizes dimensions of the fin:

	Dimension (in)
Fin Thickness	
At base	0.020"
At top	0.010"
Fin spacing	
At base	0.012"
At top	0.022"
Fin height	0.033"
Rectangular base height	0.020"
Overall width	0.180"
Overall height	0.053"
Overall length	1.500"

An Al_2O_3 slurry is prepared by mixing 7.2 g of gamma Al_2O_3 powder, 12 g of deionized H_2O and 42 g Al_2O_3 beads with 3 mm diameter. The pH value is adjusted to 3.5-4 using nitric acid. The Al_2O_3 is acidic gamma Al_2O_3 and is ground to powder smaller than 150 micrometers. The mixture is then ball-milled for 8 hours. 0.8 g of 25 wt.% Al_2O_3 sol (Sasol 14N4-25) is added to 4.2 g of the slurry with stirring.

The FeCrAlY fin is cleaned in iso-propanol for 20 min with sonication. After drying at 100 °C for 1 hour and cooling to room temperature, the fin is cleaned in 20 wt.% HNO_3 solution for 20 min with sonication. The fin is rinsed with deionized

water until the pH value is 7. After drying at 120°C for 1 hour, the fin is heated to 1000 °C in air at a heating rate of 3.5°C/min and calcined at 1000°C for 8 hours in air. The Al₂O₃ slurry is washcoated onto the fin by dipping. The excess slurry is removed by jetting air over the coated surface. The fin is dried at 120°C for 1 hour and then calcined at 450°C for 4 hours at a heating and cooling rate of 3.5°C/min. A 7.5 wt.% La(NO₃)₃ solution is impregnated onto the slurry-coated fin by dipping. The fin is dried at 120°C for 1 hour and calcined at 1000°C for 4 hours in air at a heating and cooling rate of 3.5°C/min. The slurry loading is 6.0 mg per fin. A 10 wt.% Rh(NO₃)₃ solution is dropped onto the fin and the excess solution is blown out by compressed air. The fin is dried at 120°C for 1 hour and then calcined at 1000°C for 1 hour in air. The Rh loading is 1.0 mg per fin.

The resulting fin supported catalyst is tested for partial oxidation of methane to syngas at 1 atmosphere in the pellet described in Example 3. The pellet is placed in a furnace. The temperature of the furnace is adjusted to keep the pellet skin temperature at mid-length at 805°C. The temperature of the feed stream at the inlet of furnace is at room temperature. The feed stream is preheated before entering the pellet. The length of tubing from the entrance of furnace to the pellet is 10 feet. The outlet pressure of the product stream is atmospheric pressure. The pressure drop in the pellet is the difference between the inlet and the outlet pressures. The composition of product is analyzed with a two-column Gas Chromatograph. The performance of the fin is measured in terms of CH₄ conversion, H₂ selectivity and CO selectivity. The following table summarizes catalyst performance for the fin after 115 hours of operation.

Parameter	Value
Coating Type	Powder slurry wash-coat
Fuel composition	29.6% CH ₄ , 70.4% air
Fuel contact time	3.3 ms
CH ₄ Conversion (at 850°C)	78%
H ₂ Selectivity (at 850°C)	93%
CO Selectivity (at 850°C)	93%
Pressure drop	2.8 psi

Example 5

An FeCrAlY fin is fabricated with saw-cut method and tested for catalyst performance. The following table summarizes dimensions of the fin:

		Dimension (in)
5	Fin Thickness	
	At base	0.010"
	At top	0.005"
10	Fin spacing	
	At base	0.017"
	At top	0.022"
15	Fin height	0.033"
	Rectangular base height	0.020"
20	Overall width	0.180"
	Overall height	0.053"
25	Overall length	1.500"

An Al_2O_3 slurry is prepared by mixing 7.2 g of gamma Al_2O_3 powder, 12 g of deionized H_2O and 42 g Al_2O_3 beads with 3 mm diameter. The pH value was adjusted to 3.5-4 using nitric acid. The Al_2O_3 is acidic gamma Al_2O_3 , is ground to powder smaller than 150 micrometers. The mixture is then ball-milled for 8 hours. 0.8 g of 25 wt.% Al_2O_3 sol (Sasol 14N4-25) is added to 4.2 g of the slurry with stirring.

The FeCrAlY fin is cleaned in iso-propanol for 20 min with sonication. After drying at 100°C for 1 hour and cooling to room temperature, the fin is cleaned in 20 wt.% HNO_3 solution for 20 min with sonication. The fin is then rinsed with deionized water until pH value reaches 7. After drying at 120°C for 1 hour, the fin is heated to 1000°C in air at a heating rate of 3.5°C/min and calcined at 1000°C for 8 hours in air. The Al_2O_3 slurry is washcoated onto the fin by dipping. The excess slurry is removed by jetting air over the coated surface. The fin is dried at 120°C for 1 hour and then calcined at 450°C for 4 hours at a heating and cooling rate of 3.5°C/min. 7.5 wt.% $\text{La}(\text{NO}_3)_3$ solution is impregnated onto the slurry-coated fin by dipping. The fin is dried at 120°C for 1 hour and calcined at 1000°C for 4 hours in air at a heating and cooling rate of 3.5°C/min. The slurry loading is 18.7 mg per fin. 10 wt.% $\text{Rh}(\text{NO}_3)_3$ solution is dropped onto the fin and the excess solution is blown out by compressed air. The fin is dried at 120°C for 1 hour and calcined at 1000°C for 4

hours in air. The Rh loading is 3.2 mg per fin.

The resulting fin supported catalyst is tested for partial oxidation of methane at 1 atmosphere in the pellet described in Example 3. The pellet is placed in a furnace. The catalyst is reduced with H_2 at $400^\circ C$ for 30 min before use. The feed gas compositions are 29.6% of CH_4 and 70.4% of air ($CH_4/O_2 = 2/1$), with 2372 ml/min of total flow rate (standard conditions). The contact time is 3.3. The temperature of the furnace is adjusted to keep the pellet skin temperature at mid-length at $850^\circ C$. The temperature of the feed stream at the inlet of furnace is at room temperature. The feed stream is preheated before entering pellet. The length of tubing from the entrance of furnace to the pellet is 10 feet. The outlet pressure of the product stream is atmospheric pressure. The pressure drop in the pellet is measured by a capshelic differential pressure gauge. The composition of product is analyzed with a two-column Gas Chromatograph. The performance of the fin is measured in terms of CH_4 conversion, H_2 selectivity and CO selectivity. The following table summarizes the fin supported catalyst performance after 400 hours of operation.

Parameter	Value
Coating Type	Powder slurry wash-coat
Fuel composition	29.6% CH_4 , 70.4% air
Fuel contact time	3.3 ms
CH_4 Conversion (at $850^\circ C$)	75%
H_2 Selectivity (at $850^\circ C$)	72%
CO Selectivity (at $850^\circ C$)	91%
Pressure drop	2.1 psi

Example 6

A fin having the same dimensions as the fin in Example 5 is cleaned in isopropanol for 20 min with sonication. After drying at $100^\circ C$ for 1 hour and cooling to room temperature, the fin is cleaned in 20 wt.% HNO_3 solution for 20 min with sonication. The fin is rinsed with deionized water until the pH value reaches 7. After drying at $120^\circ C$ for 1 hour, the fin is heated to $1000^\circ C$ in air at a heating rate of $3.5^\circ C/min$ and calcined at $1000^\circ C$ for 8 hours in air. A dense Al_2O_3 layer is generated after calcination. The Al_2O_3 layer functions as a protection scale and also improves the adhesion between the coating and the fin. Al_2O_3 sol (25 wt.%, Sasol 14N4-25) is coated onto the fin by dipping. The excess sol is removed by jetting air

over the coated surface. The fin is dried at 120°C for 1 hour and calcined at 450°C for 4 hours at a heating and cooling rate of 3.5°C/min. The sol coating process is repeated 3 to 4 times until 17 mg of Al_2O_3 loading per fin is achieved. 7.5 wt.% $\text{La}(\text{NO}_3)_3$ solution is impregnated onto the fin by dipping. The fin is dried at 120°C for 1 hour and calcined at 1000°C for 4 hours in air at a heating and cooling rate of 3.5°C/min. 10 wt.% $\text{Rh}(\text{NO}_3)_3$ solution is dropped onto the fin and the excess solution is blown out by compressed air. The fin is dried at 120°C for 1 hour and calcined at 500°C for 1 hour in air. The $\text{Rh}(\text{NO}_3)_3$ solution coating is repeated once and the fin is calcined at 1000°C for 4 hours. The Rh loading is 5.2 mg per fin.

The resulting fin supported catalyst is tested for partial oxidation of methane to syngas at 1 atmosphere using the pellet described in Example 3. The pellet is placed in a furnace. The catalyst is reduced with H_2 at 450°C for 30 min before use. The feed gas compositions were 29.6% of CH_4 and 70.4% of air ($\text{CH}_4/\text{O}_2 = 2/1$), with 2361 ml/min of total flow rate (standard conditions). The contact time is 3.3 ms. The temperature of the furnace is adjusted to keep the pellet skin temperature at mid-length at 800°C. The temperature of the feed stream at the inlet of the furnace is at room temperature. The feed stream is preheated before entering the pellet. The length of tubing from the entrance of furnace to the pellet is ten feet. The outlet pressure of the product stream is atmospheric pressure. The pressure drop in the pellet is measured by capshelic differential pressure gauge. The composition of product is analyzed with two-column Gas Chromatograph. The performance of the fin is measured in terms of CH_4 conversion, H_2 selectivity and CO selectivity. The performance of the fin supported catalyst after 600 hours of steady-state operation is indicated below.

Parameter	Value
Coating Type	Sol wash-coat
Fuel composition	29.6% CH_4 , 70.4% air
Fuel contact time	3.3 ms
CH_4 Conversion (at 800°C)	71%
H_2 Selectivity (at 800°C)	70%
CO Selectivity (at 800°C)	87%
Pressure drop	1.4 psi

The foregoing fin supported catalyst is tested with an n-butane and CH_4 fuel mixture. The feed gas contains 7.2% CH_4 , 7.2% n-butane and 85.6% air with a total

flow rate of 2091 ml/min. A four column gas chromatograph is used to analyze the outlet gas composition. The temperature of the furnace is adjusted to keep pellet skin temperature at mid-length at 800°C. The performance of the fin supported catalyst after 300 hours of operation is summarized below.

5

10

15

Parameter	Value
CoatingType	Powder slurry wash-coat
Fuel composition	7.5% CH ₄ , 7.5% n-butane, 85% air
Fuel contact time	3.3 ms
CH ₄ Conversion (at 800°C)	60%
n-butane conversion (at 800°C)	76%
H ₂ Selectivity (at 800°C)	77%
CO Selectivity (at 800°C)	82%
Pressure drop	1.0 psi

Example 7

20

25

30

A fin having the same dimensions as the fin in Example 3 is cleaned in isopropanol for 20 min with sonication. After drying at 100°C for 1 hour and cooling to room temperature, the fin is cleaned in 20 wt.% HNO₃ solution for 20 min with sonication. The fin is rinsed with deionized water until the pH value reaches 7. After drying at 120°C for 1 hour, the fin is heated to 1000°C in air at a heating rate of 3.5°C/min and calcined at 1000°C for 8 hours in air. A dense Al₂O₃ layer is generated after calcination. The Al₂O₃ layer functions as a protection scale and also improves the adhesion between the coating and the fin. Al₂O₃ sol (25 wt.%, Sasol 14N4-25) is coated onto the fin by dipping. The excess sol is removed by jetting air over the coated surface. The fin is dried at 120°C for 1 hour and calcined at 450°C for 4 hours at a heating and cooling rate of 3.5°C/min. The sol coating process is repeated 4 to 5 times until 22 mg of Al₂O₃ loading per fin is achieved. 7.5 wt.% La(NO₃)₃ solution is impregnated onto the fin by dipping. The fin is dried at 120°C for 1 hour and calcined at 1000°C for 4 hours in air at a heating and cooling rate of 3.5°C/min. 10 wt.% Rh(NO₃)₃ solution is dropped onto the fin and the excess solution is blown out by compressed air. The fin is dried at 120°C for 1 hour and calcined at 1000°C for 1 hour in air. The Rh loading is 1.5 mg per fin.

The resulting fin supported catalyst is tested for partial oxidation of methane to CO and H₂ at 1 atmosphere using the pellet described in Example 3. The pellet is placed in a furnace. The catalyst is reduced with H₂ at 450°C for 30 min before use. The feed gas composition contains 29.6% of CH₄ and 70.4% of air (CH₄/O₂ = 2/1), with 2030 ml/min of total flow rate (standard conditions). The temperature of the furnace is adjusted to keep the pellet skin temperature at mid-length at 850°C. The temperature of the feed stream at the inlet of the furnace is at room temperature. The feed stream is preheated before entering the pellet. The length of tubing from the entrance of furnace to the pellet is ten feet. The outlet pressure of the product stream is atmospheric pressure. The contact time is 3.3 ms. The pressure drop in the pellet, which is measured by capsuhelic differential pressure gauge, is 3.7 psi. The composition of product is analyzed with two-column Gas Chromatograph. The performance of the fin is measured in terms of CH₄ conversion, H₂ selectivity and CO selectivity. The results are shown in Fig. 9.

The test results indicate that this catalyst is stable. As shown in Fig. 9, CH₄ conversion, CO selectivity and H₂ selectivity are substantially unchanged during 840 hours time-on-stream.

Example 8

A welded Inconel reactor is fabricated to test methane combustion performance. The reactor includes two parallel channels for the combustion. Each channel is 0.160" wide and 0.025" tall. The length of reactor is 7.00". The channels are separated by 0.060" rib between them. On one side of the combustion channels, an identical pair of channels (referred as air channels) is placed to flow air required for combustion of fuel. The combustion and air channels are separated by an orifice plate with 12 circular orifices (0.012" diameter) spaced along the reactor length to distribute air into the fuel. The orifices are non-uniformly spaced to distribute air in the combustion channel. The first orifice is placed at the beginning of the reactor. The subsequent orifices are placed at distances of 0.252", 0.555", 0.905", 1.304", 1.751", 2.248", 2.794", 3.393", 4.047", 4.760", and 5.528" from the first orifice. On the other side of the combustion channel, a single heat exchange channel is placed to carry fluid which acts as a sink for combustion heat. The channel is 0.380" wide and 0.012" tall. The length of the channel is the same as the combustion channel length. The arrangement of different channels is shown in Fig. 10.

The combustion channels are coated with a combustion catalyst with solution coating. The device is first calcined in air at 1000°C for 1 hour to generate a chromia layer on the surface. The heating and cooling rate is 3.5°C/min. Subsequently, a solution containing 5.7 wt.% of Pd(NO₃)₂ and 43 wt.% of Ce(NO₃)₃·6H₂O is doped onto the channels. The excess solution is blown out by compressed air. The coated channels are then dried at 100°C for 1 hour. The Pd coating process is repeated twice. The coated channels are then calcined in air at 850°C for 1 hour.

The fuel used for the combustion is methane. The total flow rate of methane in the combustion channels is 1.0 standard liters per minute (SLPM). The total air flow rate in the air channels is 11.5 SLPM. The air is preheated to reactor temperature before mixing it in fuel. The heat sink is provided by a steam methane reforming reaction. The sink channel (referred as SMR channel) is coated with a steam methane reforming (SMR) catalyst. A mixture of 1.09 SLPM and 2.63 cc of water vapors are flowed through SMR channel. The inlet temperature of flow in SMR channel is between 800°C and 850°C. The average temperature of the combustion channel is between 850°C and 925°C. Based on the volume of combustion channel, the contact time is 4.4 ms. The methane conversion in the combustion channel is calculated as:

$$\text{CH}_4 \text{ Conversion (\%)} = (V_{\text{CH}_4, \text{ in}} - V_{\text{CH}_4, \text{ out}}) / (V_{\text{CH}_4, \text{ in}}) \times 100$$

For the combustion catalyst, the methane conversion is 30.6% at an average temperature of 862 °C. For this device an average of 9.3 W/cm² is transferred to the SMR reaction. The pressure drop in the combustion channel is between 2.5 and 5.0 psi.

Example 9

Another Inconel reactor device is fabricated to test combustion performance using a supported partial oxidation catalyst. The device has same combustion and air channel dimensions as microchannel reactor used in Example 8 except for the total partial oxidation and combustion channel length. A serrated metal sheet is used as a fin as shown in Fig. 11. Two fins are introduced at the beginning of the two partial oxidation and combustion channels. The total length of the partial oxidation and combustion channel is 8.5" to accommodate the fin, where the fin is 1.5" long

and the subsequent combustion channel is 7" long. The fin is made of FeCrAlY. The dimensions of the fin are summarized in the table below.

	Dimensions
Overall Length	1.500"
Overall width	0.180"
Overall height	0.022"
Fin thickness	0.002"
Fins per inch	60

The fins are coated with a partial oxidation catalyst to convert methane to CO and H₂ before combustion. The fins are cleaned in iso-propanol for 20 min with sonication. After drying at 100°C for 1 hour and cooling to room temperature, the fins are cleaned in 20 wt.% HNO₃ solution for 20 min with sonication. The fins are then rinsed with deionized water until pH value is 7. After drying at 120°C for 1 hour, the fins are heated to 1000 °C in air at a heating rate of 3.5 °C/min and calcined at 1000°C for 8 h in air. A dense Al₂O₃ layer is generated after the calcination and the Al₂O₃ layer functions as a protection scale and also improves the adhesion between the coating and the fins. Also, an Al₂O₃ and ZrO₂ containing slurry is prepared for coating. 10 g ZrO₂ powder, 55 g of deionized H₂O, 1.2 ml of concentrated nitric acid and 200 g Al₂O₃ beads with 3 mm diameter are mixed in a container. The mixture is then ball-milled for 2 days. After that, 2.0 g of ZrO₂ slurry, 0.54 g of gamma-Al₂O₃ powder, 0.46 g of La(NO₃)₃·6H₂O and 0.5 g of H₂O are mixed with stirring. The Al₂O₃, which is acidic gamma Al₂O₃, is ground to a powder smaller than 53 microns. Subsequently, the above Al₂O₃–ZrO₂ slurry is washcoated onto the fins by dipping. The slurry-coated fins are dried at 120°C for 1 hour and then calcined at 1000°C for 1 hour at a heating and cooling rate of 3.5°C/min. The slurry loading is 6.4 mg per fin. After that, 10 wt.% Rh(NO₃)₃ solution is dropped onto the fins and the excess solution is blown out by compressed air. Finally the slurry-coated catalysts are dried at 120°C for 1 hour and then calcined at 500°C for 1 hour in air. The Rh loading is around 0.6 mg per fin.

In the combustion channels, the orifice plate for distributing air into the fuel is modified by increasing the number of orifices to 17 and introducing non-circular orifices. The first orifice is placed in the combustion channel at a distance between 0.01" and 0.20" after the partial oxidation zone. The first orifice consists of rectangular slots with semi-circular ends of diameter 0.012". The longest length of the slot is in the direction of flow. The second orifice is equilateral triangular in shape with 0.012" side length and is placed at a distance of 0.133" from first orifice. The third & fourth orifices are of 0.012" diameter holes placed 0.267" from first orifice. The fifth orifice is again a triangular slot placed 0.386" from the first orifice. Orifice six to fifteen are circular holes with diameter 0.012" and are placed at 0.594", 0.769", 0.969", 1.168", 1.615", 2.112", 2.658", 3.257", 3.257", 3.857", 4.624" from the first orifice. Orifice sixteen and seventeen are 0.012" diameter holes placed 5.392" from first orifice. This pattern of orifices provides an ideal oxygen equivalence ratio of 0.5, defined as:

$$\xi_{O_2} = \frac{Y_{O_2}}{Y_{O_2} + Y_{O_2,stoic}}$$

Where Y_{O_2} is the mole fraction of oxygen and $Y_{O_2,stoic}$ is stoichiometric oxygen mole fraction necessary for complete combustion.

The combustion channels are coated with combustion catalyst. The device is first calcined in air at 1000°C for 3 h to generate a chromia layer on the surface. The heating and cooling rate is 3.5°C/min. 10 wt.% $Rh(NO_3)_3$ solution is then dropped onto the combustion channels and the excess solution is blown out by compressed air. After drying at 100°C for 1 hour, the coated channels are calcined at 800°C for 1 hour in air. Subsequently, a solution containing 5.7 wt.% of $Pd(NO_3)_2$ and 43 wt.% of $Ce(NO_3)_3 \cdot 6H_2O$ is doped onto the channels. The excess solution is blown out by compressed air. The coated channels are then dried at 100°C for 1 hour. The Pd coating process is repeated once. The coated channels are then calcined at 1000 °C for 1 h. Finally, 10 wt.% $Pt(NH_3)_4(NO_3)_2$ solution is dropped onto the channels. After drying at 100°C for 1 hour, the coated channels are calcined at 900°C for 1 hour in air.

The reactor performance with integrated partial oxidation and combustion reaction is tested. The total flow rate of methane in the two combustion channels is 1.33 SLPM. The methane is premixed with air to have $CH_4:O_2$ ratio of 2:1 in the

partial oxidation channels. The total flow rate of air in the air channels is 10.9 SLPM. The air is preheated to the reactor temperature before mixing into fuel. The heat sink is provided by a steam methane reforming reaction. The sink channel (referred as SMR channel) is coated with steam methane reforming (SMR) catalyst. A mixture
5 of 2.18 SLPM and 5.27 cc of water vapors flow through the SMR channel. The inlet temperature of flow in SMR channel is between 800°C and 850°C. The average partial oxidation zone temperature is between 750°C and 800°C and average combustion zone temperature is between 850°C and 925°C. Based on the volume of combustion channels, the contact time in combustion channels is 4.5 ms. The
10 total CH₄ conversion is 92.2%, an increase of 61.6% as compared to that without partial oxidation catalyst. This demonstrates that partial oxidation assists methane combustion significantly. For this device an average of 18.8 W/cm² is transferred to the SMR reaction. The pressure drop in the combustion channel is between 2.5 and 5.0 psi.

What is claimed is:

1. A process for converting a hydrocarbon reactant to a product comprising H₂ and CO, the process comprising:

(A) flowing a reactant composition comprising the hydrocarbon reactant and oxygen or a source of oxygen through a microchannel reactor in contact with a catalyst under reaction conditions to convert the reactant composition to the product, the hydrocarbon reactant comprising methane, the catalyst comprising a composition represented by the formula



wherein

M¹ is Rh, Ni, Pd, Pt, Ru, Co or a mixture of two or more thereof;

M² is Ce, Pr, Tb or a mixture of two or more thereof;

M³ is La, Ba, Zr, Mg, Ca or a mixture of two or more thereof;

a is a number in the range of about 0.0001 to about 1;

b is a number in the range of zero to about 0.9999;

c is a number in the range of about 0.0001 to about 0.9999;

d is a number in the range of about 0.0001 to about 0.9999; and

x is the number of oxygens needed to fulfill the valency requirements of the elements present;

the catalyst being coated on an interior wall of the process microchannel, or supported on a foam, felt, wad or fin positioned within the process microchannel.

2. A catalyst comprising a composition represented by the formula



wherein

M¹ is Rh, Ni, Pd, Pt, Ru, Co or a mixture of two or more thereof;

M² is Ce, Pr, Tb or a mixture of two or more thereof;

M³ is La, Ba, Zr, Mg, Ca or a mixture of two or more thereof;

a is a number in the range of about 0.0001 to about 1;

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b is a number in the range of zero to about 0.9999;

c is a number in the range of about 0.0001 to about 0.9999;

d is a number in the range of about 0.0001 to about 0.9999; and

x is the number of oxygens needed to fulfill the valency requirements of the elements present;

the catalyst being coated on a substrate or supported on a foam, felt, wad or fin.

3. The catalyst of claim 2 wherein M^1 is Rh or Ni.

4. The catalyst of claim 2 wherein M^1 is Rh.

5. The catalyst of claim 2 wherein M^3 is La or Mg.

6. A catalyst comprising a composition represented by the formula



wherein

a is a number in the range of about 0.0001 to about 0.9999;

c is a number in the range of about 0.0001 to about 0.9999;

d is a number in the range of about 0.0001 to about 0.9999; and

x is the number of oxygens needed to fulfill the valency requirements of the elements present.

7. A process for making a supported catalyst, comprising:

(A) applying a layer of Al_2O_3 over at least part of a support structure;

(B) calcining the treated support structure formed in step (A);

(C) applying a promoter or stabilizer to the surface of the calcined support structure formed in step (B) to form a treated support structure, the promoter or stabilizer comprising La, Ba, Zr, Mg, Ca, or an oxide or nitrate thereof, or a mixture of two or more thereof;

- (D) calcining the treated support structure formed in step (C);
- (E) applying a catalytic metal or oxide or nitrate thereof to the surface of the calcined support structure formed in step (D) to form a treated support structure, the catalytic metal comprising Rh, Ni, Pd, Pt, Ru, Co or a mixture of two or more thereof; and
- (F) calcining the treated support structure formed in step (E) to form the supported catalyst.

8. The process of claim 7 wherein the supported catalyst formed in step (F) is reduced in hydrogen.

9. The process of claim 7 wherein the support structure is made of a material comprising: steel; aluminum; titanium; iron; nickel; platinum; rhodium; copper; chromium; brass; an alloy of any of the foregoing metals; a polymer; ceramics; glass; a composite comprising polymer and fiberglass; quartz; silicon; or a combination of two or more thereof.

10. The process of claim 7 wherein the support structure is made of an alloy comprising Fe, Cr, Al and Y, and the native oxide layer comprises Al_2O_3 .

11. The process of claim 7 wherein the support structure is made of an alloy comprising Ni, Cr and Fe, and the native oxide layer comprises Cr_2O_3 .

12. The process of claim 7 wherein the promoter or stabilizer comprises La or Mg.

13. The process of claim 7 wherein the promoter or stabilizer comprises La.

14. The process of claim 7 wherein the catalytic metal comprises Rh.

15. The process of claim 7 wherein prior to step (A) the support structure is heated to a temperature in the range of about 300°C to about 1400°C for about 0.1 to about 1000 hours.

16. The process of claim 7 wherein during step (A) a slurry comprising Al_2O_3 is applied over the native oxide layer.

17. The process of claim 7 wherein during step (A) a colloidal dispersion comprising Al_2O_3 is applied over the native oxide layer.

18. The process of claim 7 wherein during step (B) the treated support structure is calcined at a temperature in the range of about 150°C to about 1200°C for about 0.1 to about 1000 hours.

19. The process of claim 7 wherein during step (C) a solution comprising $\text{La}(\text{NO}_3)_3$ is applied to the surface of the calcined support structure.

20. The process of claim 7 wherein during step (D) the treated support structure is calcined at a temperature in the range of about 150°C to about 1200°C for about 0.1 to about 1000 hours.

21. The process of claim 7 wherein during step (E) a composition comprising $\text{Rh}(\text{NO}_3)_3$ is applied to the surface of the calcined support structure.

22. The process of claim 7 wherein during step (F) the treated support structure is calcined at a temperature in the range of about 150°C to about 1200°C for about 0.1 to about 1000 hours.

23. The catalyst of claim 2 wherein the catalyst is represented by the formula $\text{Rh}/\text{LaAl}_{11}\text{O}_{18}$ or Rh/LaAlO_3 .

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Figures: 10, 11

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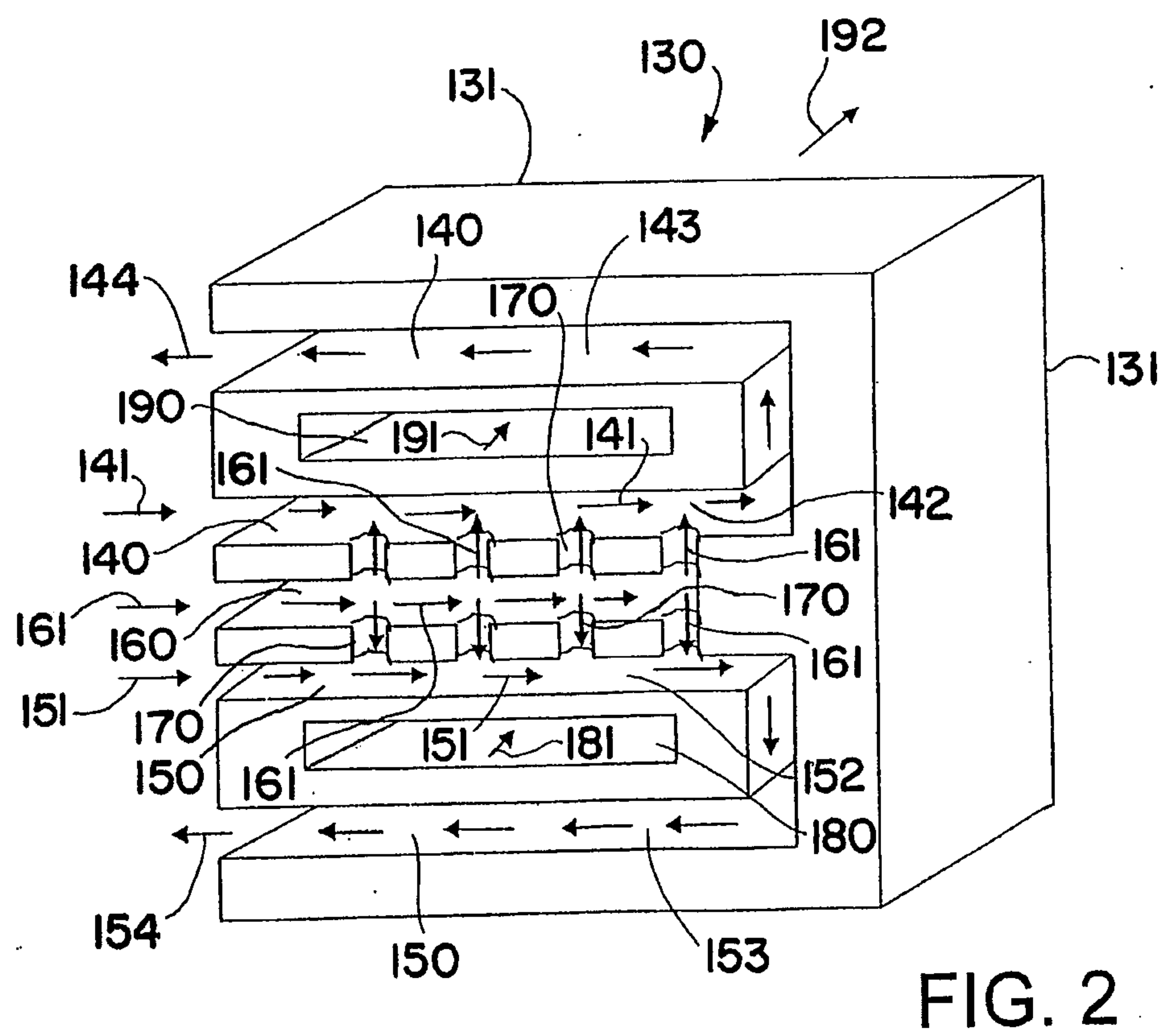
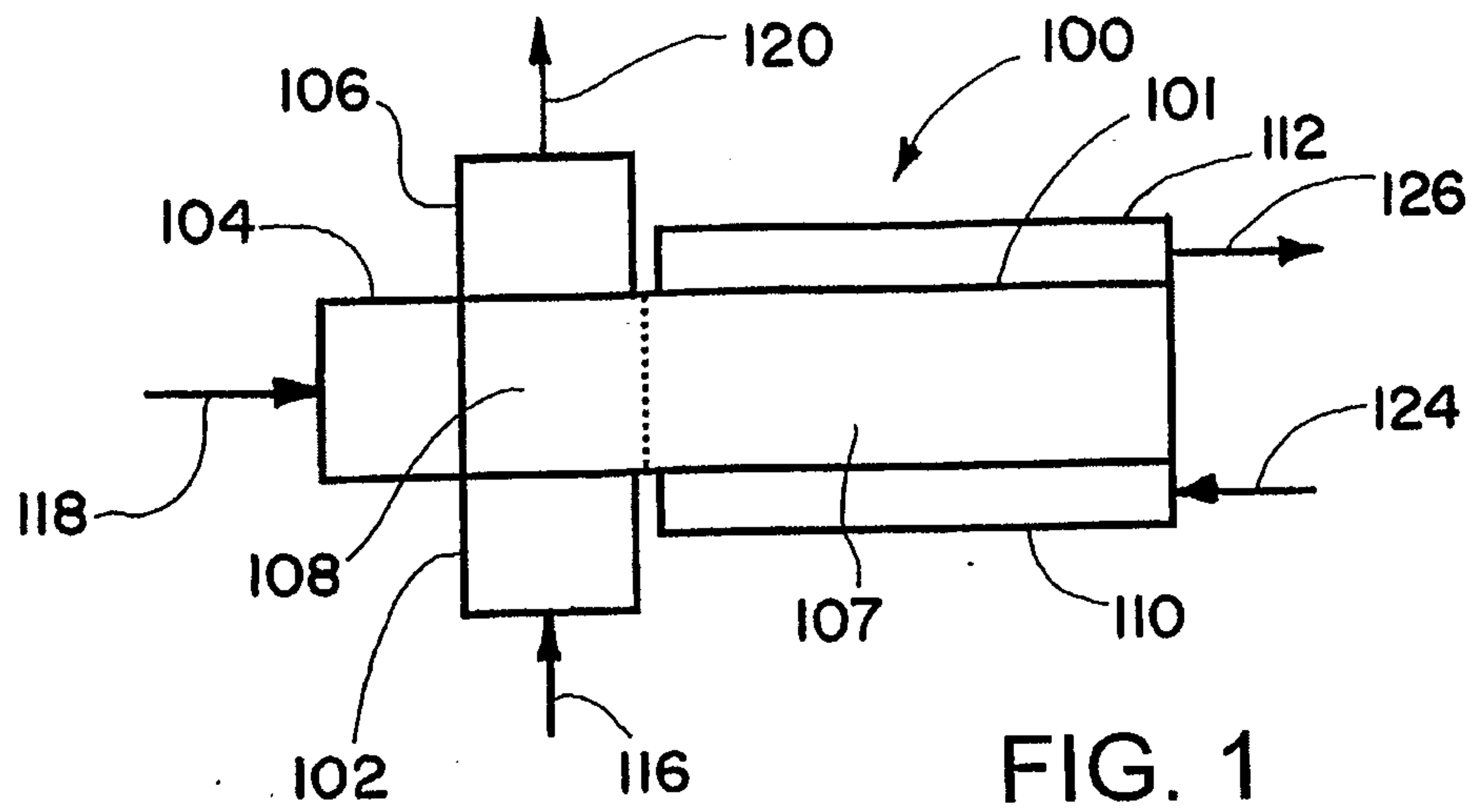
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Drawings

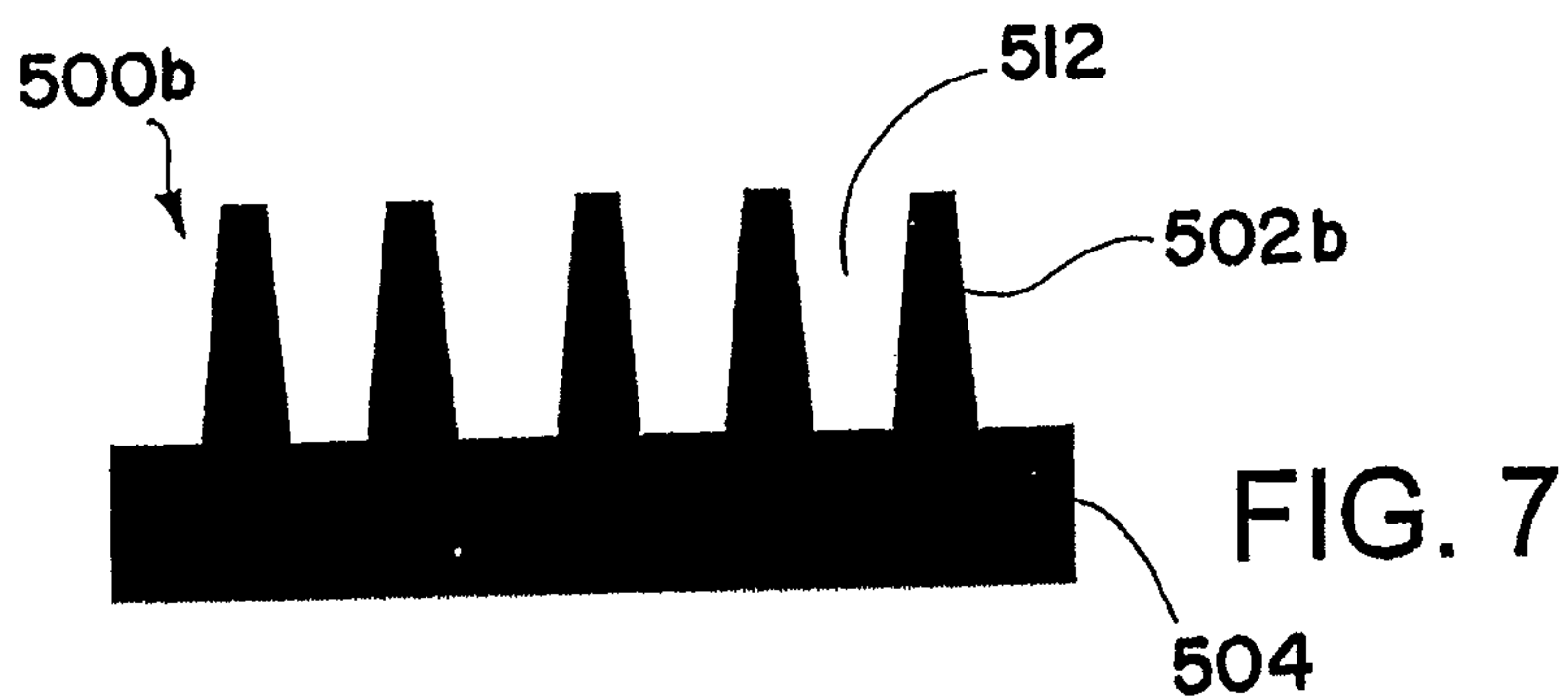
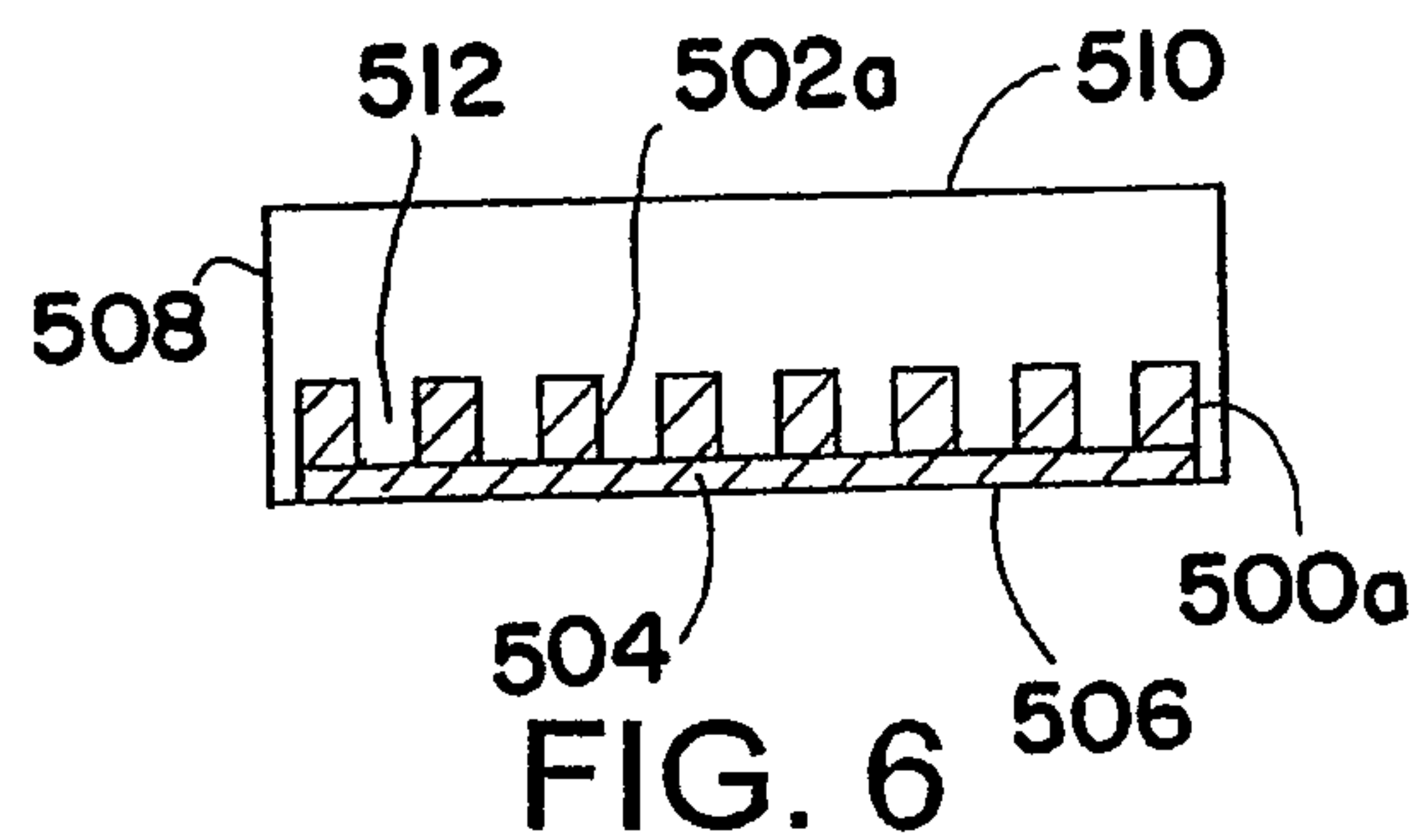
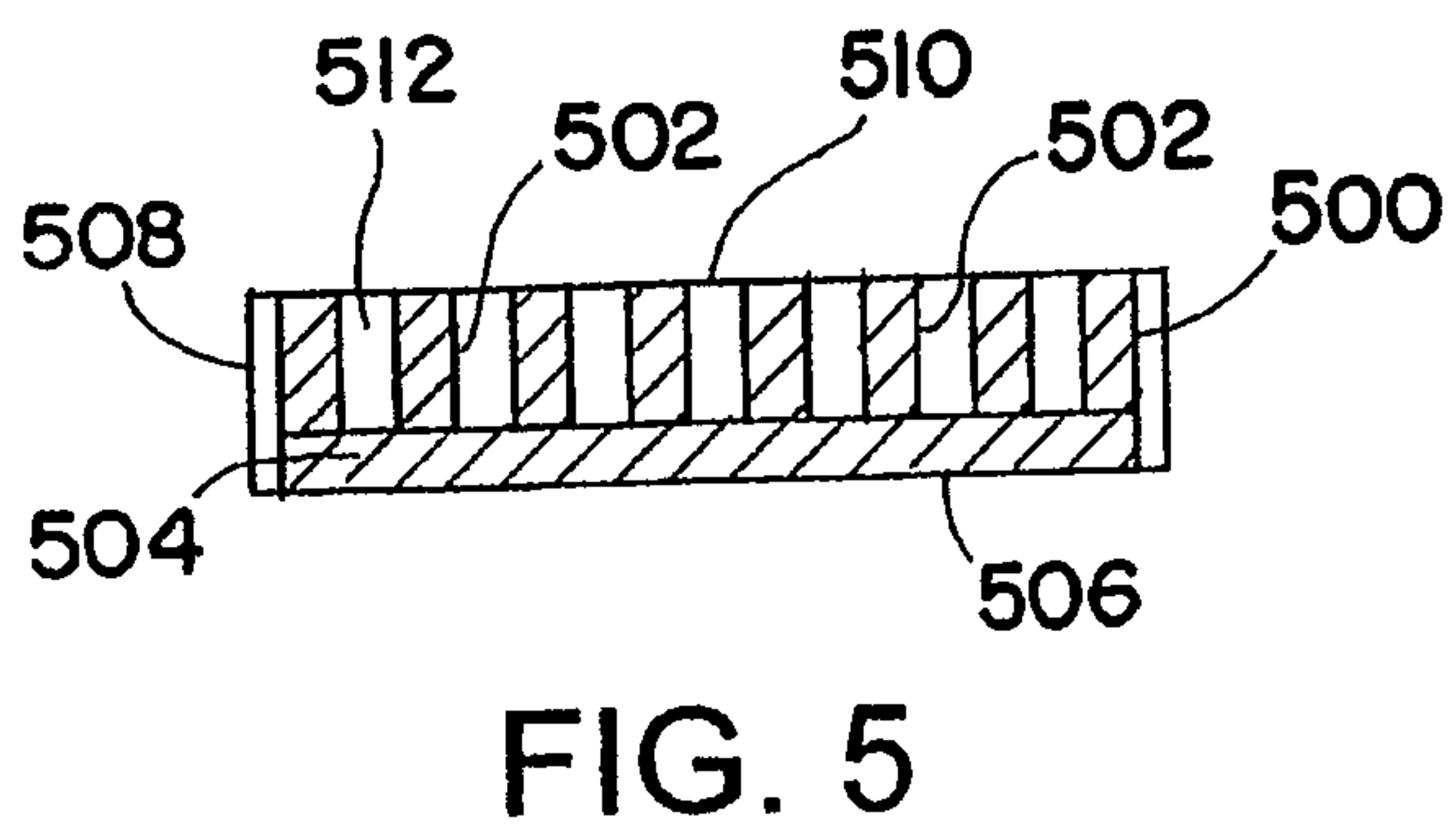
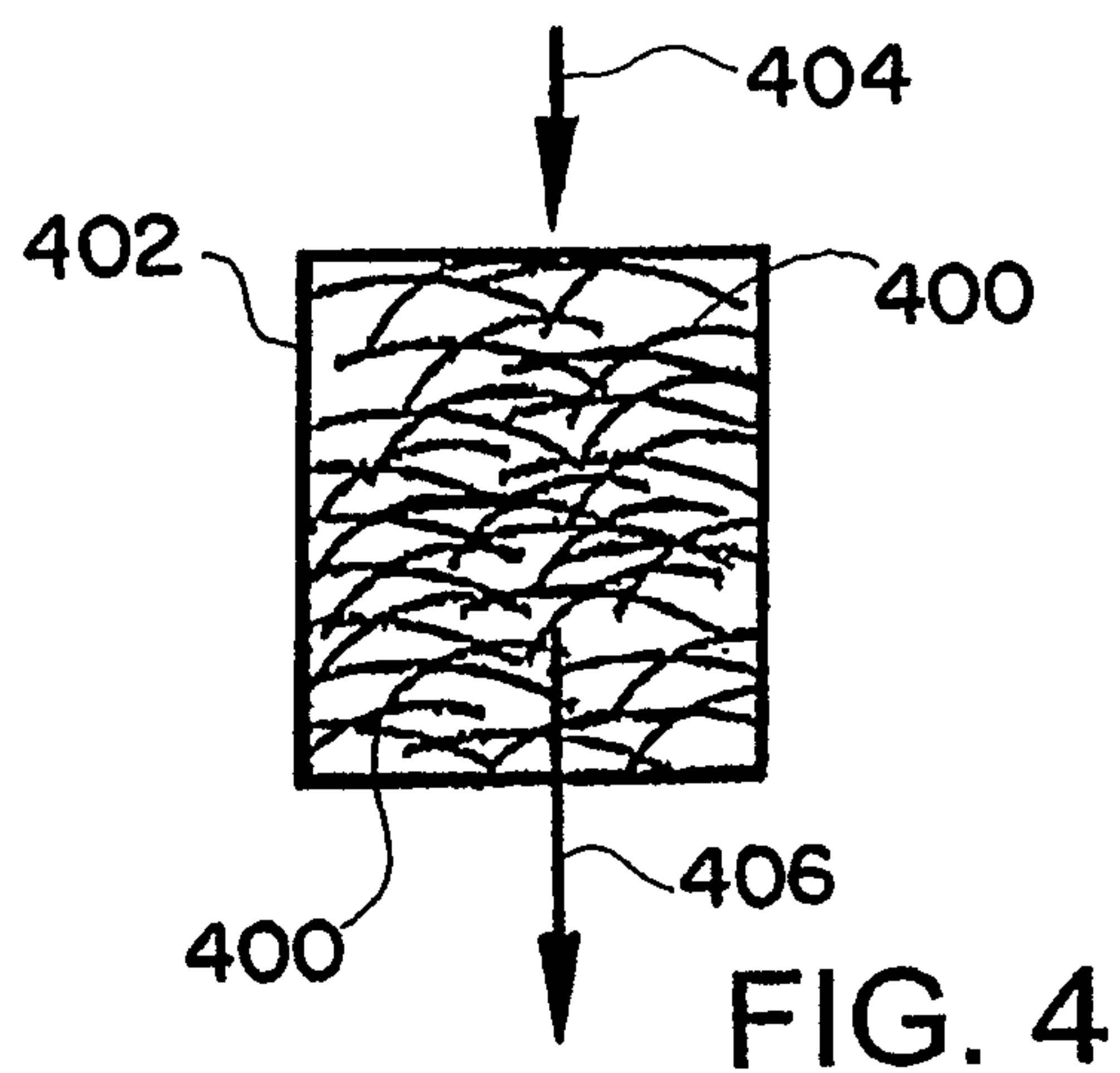
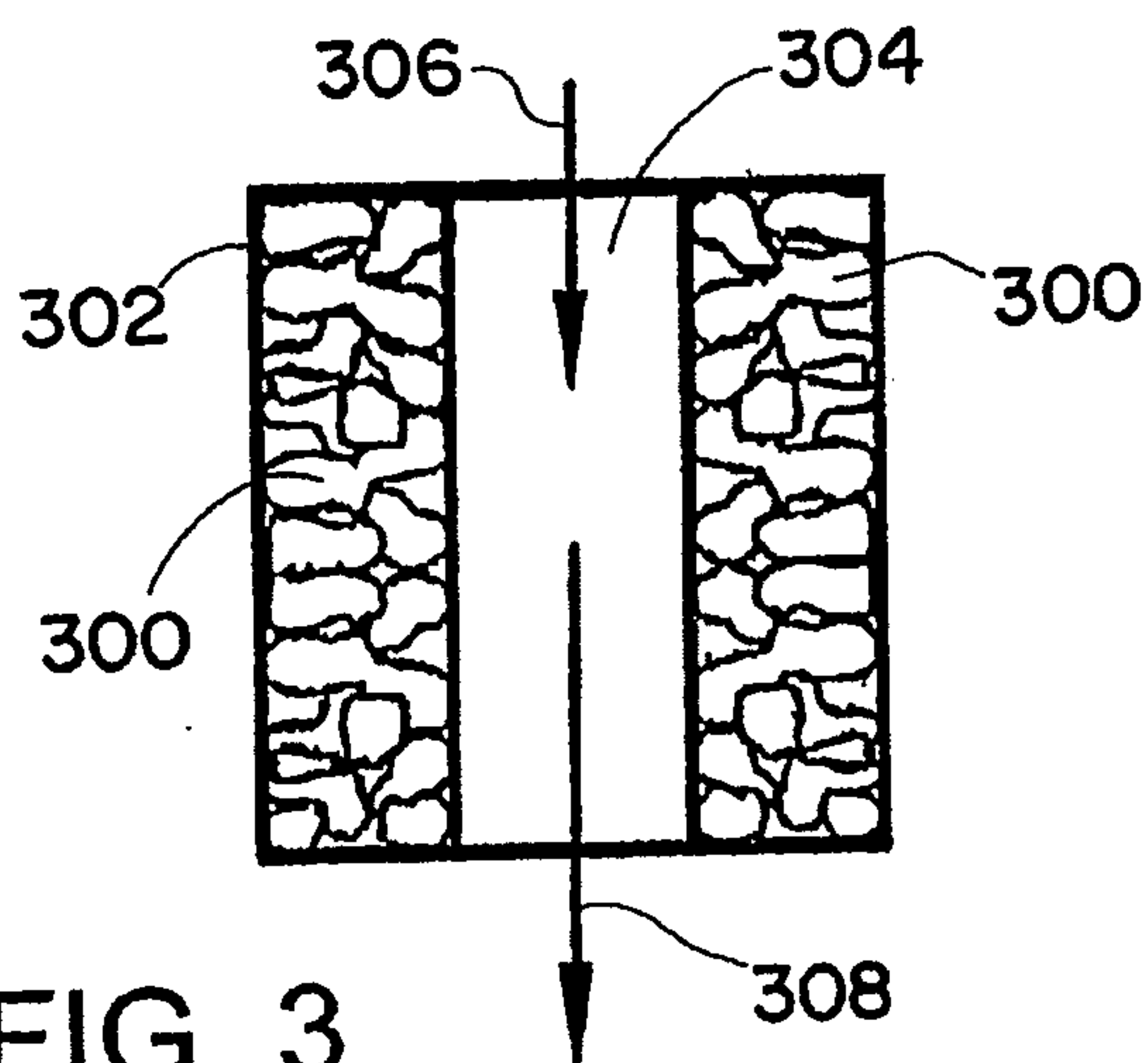
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**Lifetime of Rh/La₂O₃-Al₂O₃ powder catalyst for
partial oxidation of methane**

T = 700 °C, 30 mg catalyst, 29.6% CH₄, 70.4% air, GHSV = 5.8 X 10⁶ h⁻¹

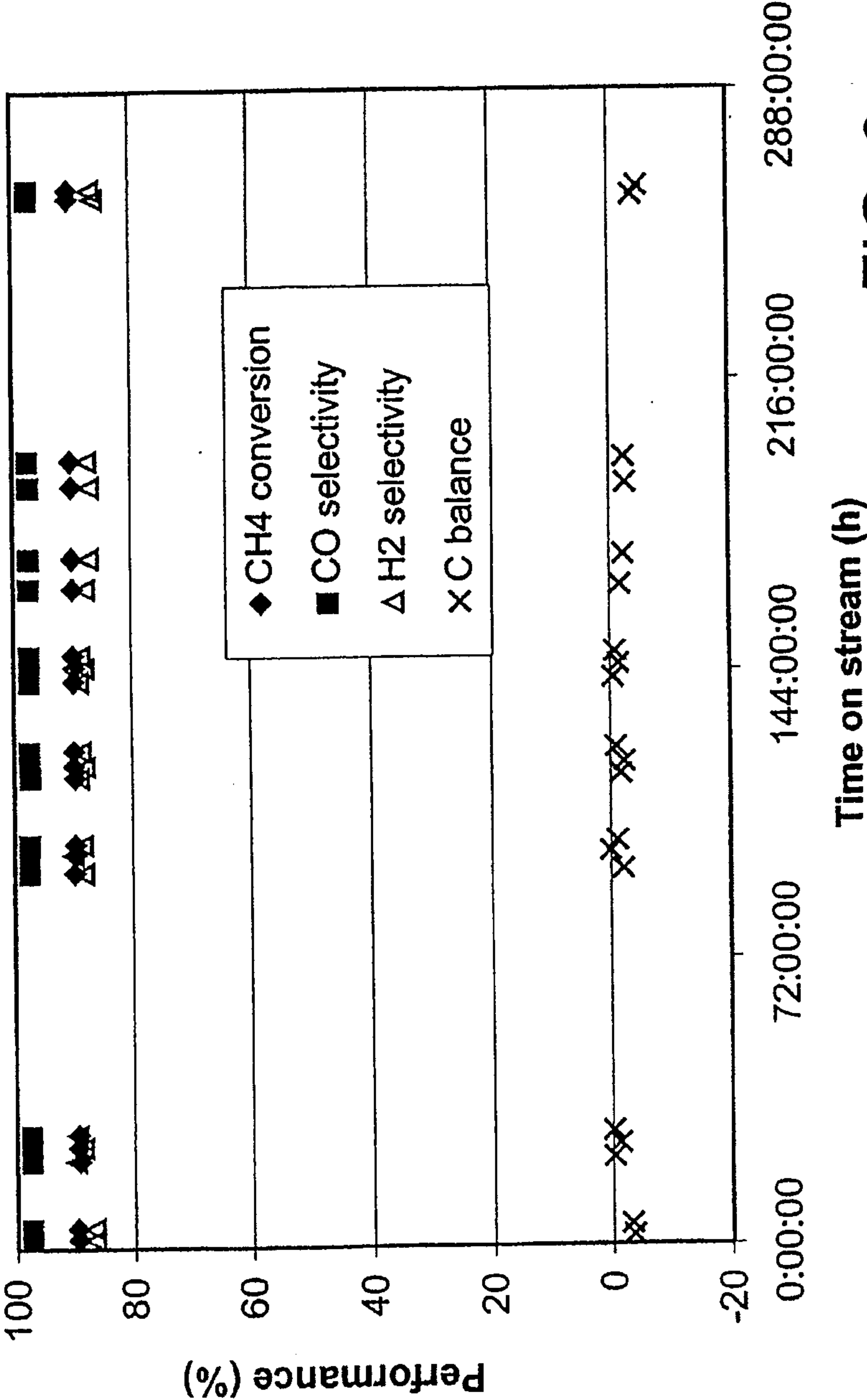


FIG. 8

Life-time of Rh/La₂O₃-Al₂O₃/fin for partial oxidation of methane
Reaction conditions: T = 850 C, CH₄/O₂ = 2/1, C.T. = 3.3 ms

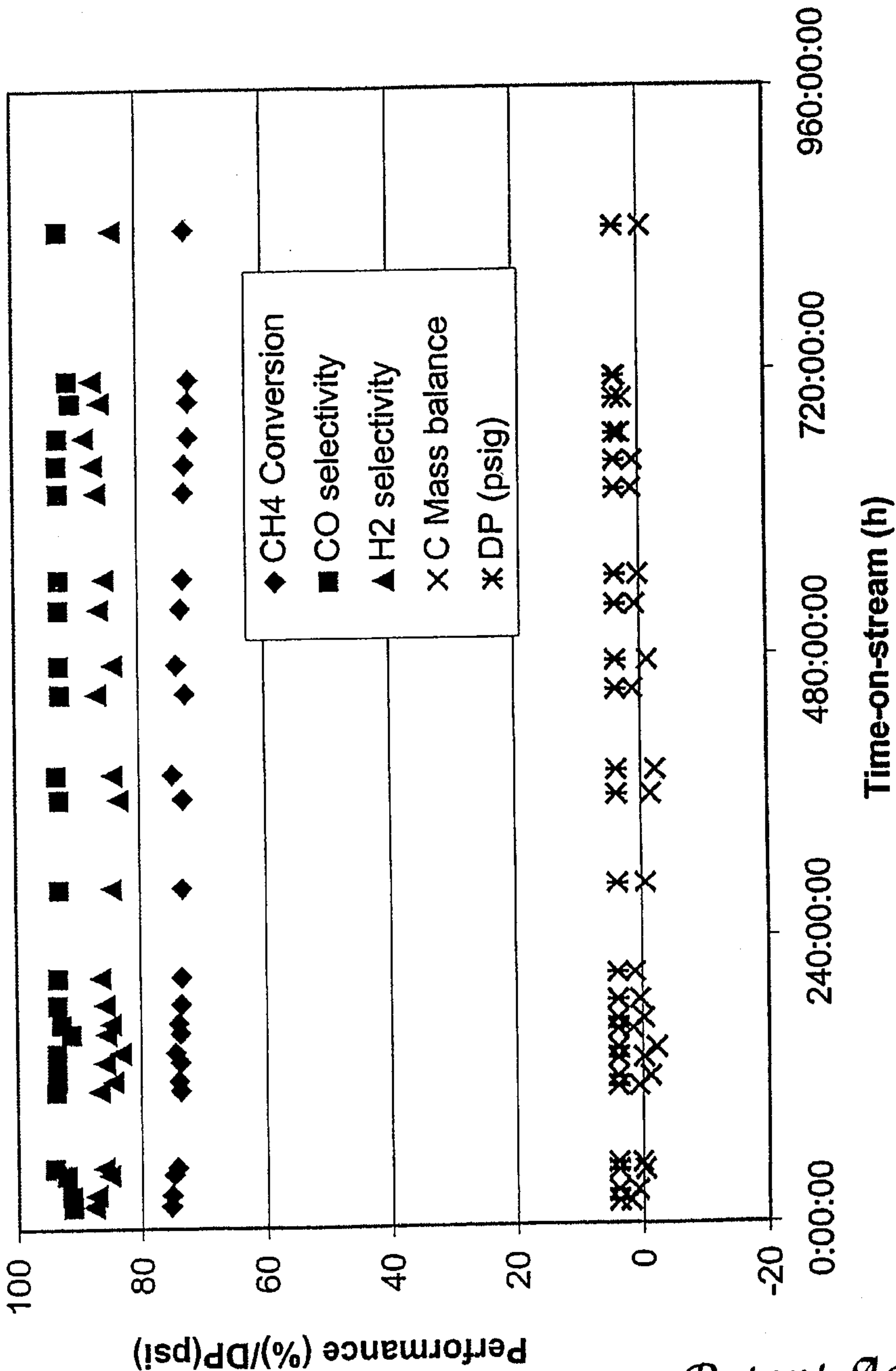


FIG. 9